HETEROCYCLIC ANALOGUES OF AZULENE

by

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TO

MY PARENTS

AND TO

MY WIFE

A C K N O W L E D G E M E N T S

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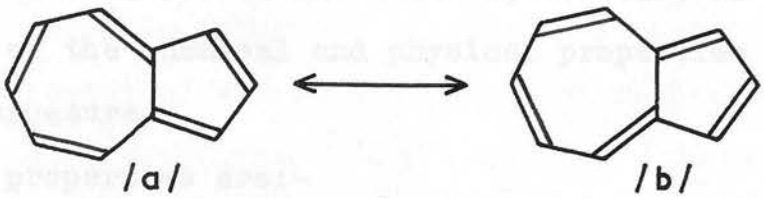
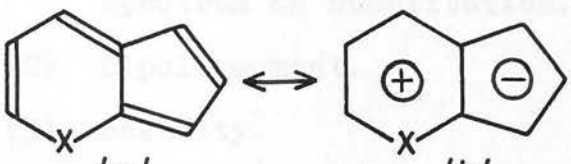
C O N T E N T S

INTRODUCTION AND DISCUSSION

The replacement of the group -CH=CH- of an aromatic ring by an atom X capable of providing two mobile electrons results in a molecule which more or less retains the aromatic character of the parent. Azulene I should thus give rise to the heterocyclic systems II and III which may be represented as resonance hybrids between the Kekulé forms (a) and the dipolar forms (b), in which each ring has a share of an aromatic sextet.



I



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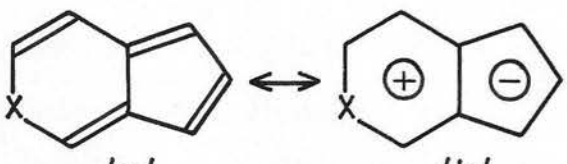


III

The structure of these systems can best be discussed by direct comparison with azulene.

Derivatives of azulene have been known for many years but its structure and properties have been revealed comparatively recently. To the blue material present in certain essential oils the generic name "azulene" was given by Piesse in 1863 (Chem.News, 1863, 8, 245). Sherndal (J.A.C.S., 1915, 37, 167, 1537) observed that the azulenes could be extracted into mineral acids and were regenerated on dilution. The basic structure,

however, was not solved until 1936 when Pfau and Plattner established that azulene contained fused five- and seven-membered rings. They represented it as a resonance hybrid of two classical forms I (a) and (b). In the same year they synthesised 4-methyl-azulene (Helv.Chim.Acta, 1936, 19, 858) and in 1937 followed this with the synthesis of the parent compound (ibid., 1937, 20, 224).

Difficulties were soon encountered, however, in the relationship of the chemical and physical properties to an acceptable structure.

The physical properties are:-

(1) Intense blue colour and characteristic changes in the visible spectrum on substitution.

(2) Dipole moment.

(3) Basicity.

The chemical properties are:-

(1) Electrophilic substitution in positions 1 (3).

(2) Nucleophilic substitution in positions 4 (8).

The azulene molecule has considerable stability shown by its successful preparation by high temperature dehydrogenation of its hydro-derivatives. This tendency to be formed and to undergo substitution rather than addition reactions may be regarded as evidence of aromaticity.

Azulene can thus be regarded as a "non-classical aromatic" system. Such systems do not contain any benzenoid rings, or else

these are not present alone, and yet they possess great enough resonance energies to be classed alongside benzene, naphthalene, etc., as aromatic compounds.

It should be noted, however, that resonance energy is the property of the ground state of a molecule in isolation and with no more than a secondary influence on reactivity. The resonance energy of benzene is 36 kcal./mole in contrast to 61 kcal./mole in naphthalene (Klages, Chem.Ber., 1949, 82, 358) and it increases in the larger aromatic molecules roughly in proportion to the number of π electrons, but at the same time higher homologues are generally more reactive, thus showing that inertness and resonance stabilisation do not always go together. It is also not a very well defined quantity and various estimates are given even in the best studied examples. Despite its limitations, however, the evaluation of the resonance energy is often useful and in the known aromatic compounds there is probably no other quantity which so closely parallels chemical experience. Turner et al. (J.A.C.S., 1957, 79, 4127) give the resonance energy of azulene as 30.5 kcal./mole. This value is a difference between the true π resonance energy and σ strain energy in the five- and seven-membered rings. If 10 kcal./mole is allowed for the strain energy, the net resonance energy referable only to electron effects is 40.5 kcal./mole, or 4 per π electron, compared with 5-7 for benzenoid hydrocarbons (Craig, "Non-Benzenoid Aromatic Compounds"; Weltner, J.A.C.S., 1953, 75, 4224).

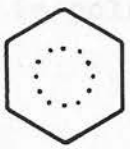
The basis of our present concept of aromaticity was proposed by Robinson in 1925. In his classical paper (J., 1925, 127, 1604) he was the first to refer to the six mobile benzene electrons as the "aromatic sextet" which resisted disruption and was responsible for the chief characteristics of the aromatic systems. Robinson also considered that the number of electrons in non-classical aromatic systems had to be such that structures could be drawn with sextets in each ring. Long before the advent of the theory of resonance he suggested that, "... there is a very large class of substances which can ... be regarded as normally occupying an intermediate position between a fully polarised aromatic phase and a neutralised quinonoid (covalent) phase ...". Over thirty years later, Robinson, in discussing the past and present meaning of the term "aromatic character" and the fact that there is still no general concensus of opinion with regard to the limits of any appropriate generalisation, states, "... the aromatic sextet has proved a useful hall-mark for the great majority of cases, but it is only one of several similar electron groups which confer a special kind of stability on the molecule. Surely the carboxyl ion is aromatic in the broader sense of the term based on theory, and perhaps we need a new word in order to enable us to say more exactly what ... we mean".
("Foreword" in "Non-benzenoid Aromatic Compounds", edited by Ginsburg.)

Robinson's concept of an "aromatic sextet" of mobile electrons as a necessity for aromaticity has since been extended by Hückel, Pauling and others who demonstrated its compatibility with the quantum physics of electrons. Hückel (Z.Phys., 1931, 70, 204) using molecular orbital theory showed that for a carbocyclic molecule to be aromatic it must be a planar conjugated polyolefin with a total of $(4n + 2)$ π electrons, where n = 1, 2, 3, etc. He thus suggested that there was a fundamental cleavage between molecules with 4n and $(4n + 2)$ π electrons. In later years it has been recognized that the form of molecular orbital theory upon which his rule is founded is a first approximation and that it is just in the 4n-electron case that a second approximation is most needed (Wheland, Proc.Roy.Soc., 1938, A164, 397; Craig, idem., 1950, A202, 498). However, in the qualitative sense, nothing has changed the correctness of Hückel's forecast in the field of monocyclic π-electronic systems. As was pointed out by Boekelheide and co-workers (J.A.C.S., 1958, 80, 2020; ibid., 1959, 81, 1459) and others the rule is not really applicable to polycyclic compounds and a separate molecular orbital calculation should be made for each compound in the endeavour to predict its possible aromatic character. It is of interest to note in this connection that in all the known polycyclic aromatic compounds consisting only of fused benzene rings, the periphery contains $(4n + 2)$ carbon atoms associated with the same number of π electrons, e.g.,

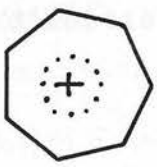
anthracene, phenanthrene, and pyrene all have a periphery of 14 carbon atoms, coronene has 18, and so on. A large number of polycyclic hydrocarbons which do not possess a periphery associated with $(4n + 2)$ π electrons are incompletely aromatic; for example the peripheral double bond in the five-membered ring of acenaphthylene (11 peripheral π electrons) shows olefinic properties.

Molecular orbital calculations of the stabilities of the five- and seven-membered ring ions (Roberts, Streitwieser and Regan, J.A.C.S., 1952, 74, 4579) are in agreement with Hückel's requirements for aromaticity for they predicted that the five-membered ring anion and the seven-membered ring cation would be more stable than the other possible neutral or ionic species. Doering and Knox (J.A.C.S., 1954, 76, 3203) regard the cyclopentadienyl anion, benzene and the cycloheptatrienylium cation, each possessing six π electrons, as a triad of stable aromatic systems.

IV



V



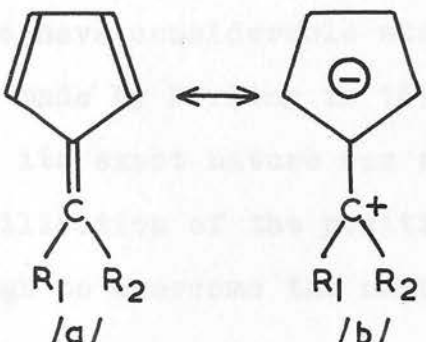
VI

They can be formulated as IV, V and VI to represent a symmetrical distribution of electrons and in the two ions to indicate delocalisation of the charge throughout the molecular orbitals. These are composed of as many π orbitals as there are carbon atoms

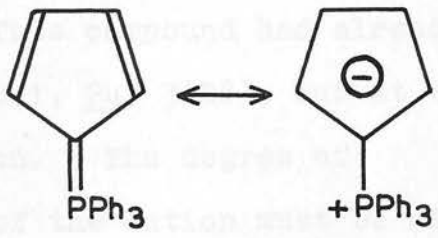
in the polygons and are occupied by a number of electrons equal to the number of carbon atoms plus or minus one, according to the overall charge of the system.

The cyclopentadienyl anion and the cycloheptatrienylium cation are thus electronically analogous to benzene and possess the requisite symmetry for aromaticity. Within recent years much interest has centred on such non-classical aromatic systems and their stability is now well recognized.

Cyclopentadiene itself is completely devoid of aromaticity and indeed, the unsaturated character of the conjugated diene system is here enhanced by the ring strain. The difference in resonance energy between the diene and its anion was calculated to be 39 kcal./mole (Roberts, Streitwieser and Regan, J.A.C.S., 1952, 74, 4579). This anionic stability has long been known in that cyclopentadiene forms stable metal salts (Thiele, Ber., 1900, 33, 666; ibid., 1901, 34, 68). The five-membered ring can also become aromatic on addition of an exocyclic double bond as in VII, provided that it is polarised in the direction indicated by VII (b).



VII



VIII

The condensation of cyclopentadiene with aldehydes and ketones to form fulvenes VII is considered to occur through preliminary formation of the cyclopentadienyl anion. The dipole moment (1.1 D. for VII, $R_1=R_2=H$; Thiec and Wiemann, Bull.soc.chim. France, 1956, 177), resonance energy (approximately 12 kcal./mole for the fulvene system; Day and Oestreich, J.Org.Chem., 1957, 22, 214), and colour of the fulvenes suggest that there is an appreciable contribution to the resonance hybrid from dipolar form VII (b). Examples of the most aromatic compounds of this type, those where an electron-donating atom or group is attached to the five-membered ring, have only recently been described, e.g., Ramirez and Levy (J.A.C.S., 1957, 79, 67) have reported the synthesis of intensely coloured triphenylphosphonium cyclopentadienylide VIII.

The stability of the anion is further illustrated by the existence of dicyclopentadienyliron, "ferrocene", (Kealy and Pauson, Nature, 1951, 168, 1039).

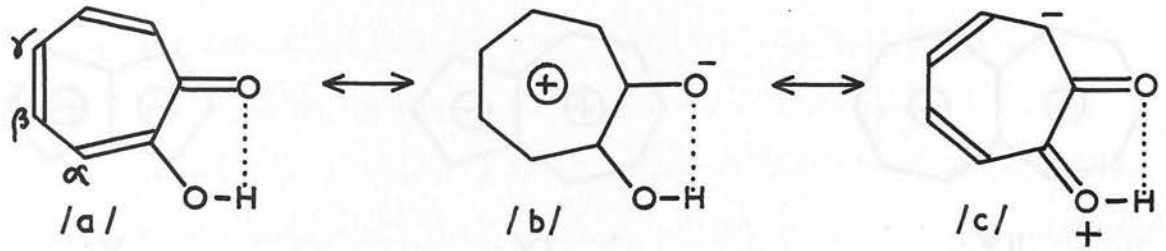
In support of their view of the cycloheptatrienylium (tropylium) cation VI as an analogue of benzene, Doering and Knox (J.A.C.S., 1954, 76, 3203) prepared the bromide and found it to have considerable stability. This compound had already been made by Merling in 1891 (Ber., 1891, 24, 3108), but at that time its exact nature was still unknown. The degree of stabilisation of the positive charge of the cation must be high enough to overcome the natural covalent tendency of the C - Br

bond, for it is soluble in water and reacts immediately with silver nitrate. Tropylium ion behaves as a Lewis acid in water and is in equilibrium with the carbinol and hydronium ion.

$$C_7H_7^+ + 2H_2O \rightleftharpoons C_7H_7OH + H_3O^+$$

The acidity in water is approximately that of acetic acid (Doering and Knox, loc. cit.). The fact that there is no common band in the infrared and Raman spectra of tropylium bromide indicates the highly symmetrical character of tropylium ion (Fateley and Lippincott, J.A.C.S., 1955, 77, 249). Structures based on this cation are to be found in tropolone and tropone.

Tropolone IX is a stable compound showing more fully developed aromatic character than tropone and its aromaticity was predicted from theoretical considerations by Dewar (Nature, 1945, 155, 50).

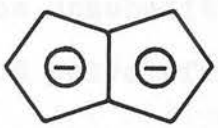


IX

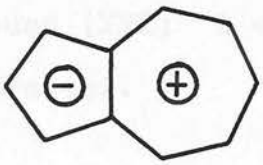
It does not behave as a ketone but rather as a phenol and readily undergoes electrophilic substitution (at α and γ positions). The physical methods of analysis show it to be an almost regular

heptagon of bond length 1.40Å; it has a dipole moment of 3.53D. (Kurita, C.A., 1955, 49, 9989) and resonance energy of 21 kcal./mole. Tropolone has thus been represented as a resonance hybrid of IX (a), (b) and (c) (Doering and Knox, 1952, 74, 5683; Kubo, Nozoe and Kurita, Nature, 1951, 167, 688).

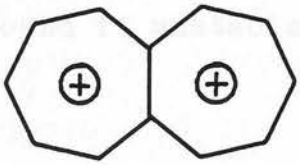
In the monocyclic systems it has been seen that the stable conditions are the triad IV, V and VI. A bicyclic aromatic compound naphthalene represents a stable fusion of two neutral benzene rings V and of the ten π electrons available to the system each ring has an equal share and effectively a full complement of six π electrons: four unshared and two shared. The equivalent condition for two five-membered rings IV is the dianion X, in which each ring also has an equal share of the system's ten π electrons and effectively the required sextet, but since the two rings have identical electronic requirements, mutual satisfaction is impossible.



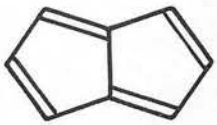
X



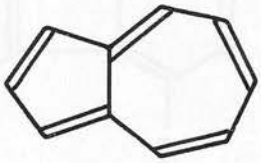
XI



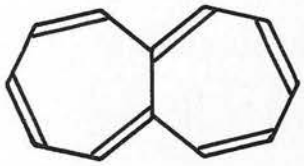
XII



XIII



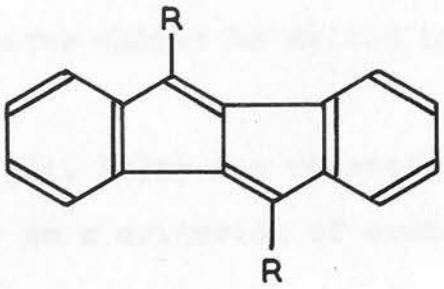
XIV



XV

The hypothetical pentalene XIII has a total of eight π electrons and as was first pointed out by Armit and Robinson (J., 1925, 127, 1604), there is no possible way in which each ring can attain the aromatic sextet. These two rings can therefore never attain a state of neutrality whilst at the same time satisfying Robinson's condition for aromaticity. The same holds for the two seven-membered rings VI since fusion results in a dication XII and in neutral heptalene XV, with a total of 12 π electrons, the two rings can never achieve the stable sextet structure.

The incompatibility of such unions is shown in that all attempted syntheses of unsubstituted pentalene and heptalene have so far failed (e.g., Pentalene: Barrett and Linstead, J., 1936, 611; Roberts and Gorham, J.A.C.S., 1952, 74, 2278; Blood and Linstead, J., 1952, 2255. Heptalene: Aspinall and Baker, J., 1950, 743; Horn and Rapson, J., 1949, 2421). The derivatives of 1,2,4,5-dibenzopentalene XVI have been known for many years and in 1952 Blood and Linstead (J., 1952, 2263) succeeded in preparing the unsubstituted compound (XVI; R = H) and found it unstable and polyolefinic in character.



XVI

Dimethyldibenzopentalene (XVI; R = CH_3) appears to be the simplest of the very few known compounds containing the pentalene ring system to have had its diamagnetic susceptibility recorded (Bergmann et al., J.chim.phys., 1952, 49, 474) and to which this physical criterion of aromaticity can be applied. If the dibenzopentalene nucleus were aromatic its susceptibility exaltation would be expected to be close to that of chrysene (about 68 units). Alternatively, if the dibenzopentalene nucleus consisted of two benzene rings held by a non-aromatic pentalene bridge making no contribution to the susceptibility exaltation, but not interfering with that of the benzene rings, then the measured exaltation would be 37 units (equal to two benzenes). Measurement gives 28 units and appears to show that the pentalene nucleus has no peripheral conjugation of the aromatic type and further that there is some interference by the five-membered rings with the benzenoid resonance itself. This establishes clearly that the pentalene nucleus is non-aromatic.

It should be noted here that, according to both valence bond and molecular orbital methods, pentalene and heptalene should have large resonance energies. It is therefore apparent that the problem of the conditions of structure required for the development of aromatic character cannot be solved by simple theories of π-electron energies.

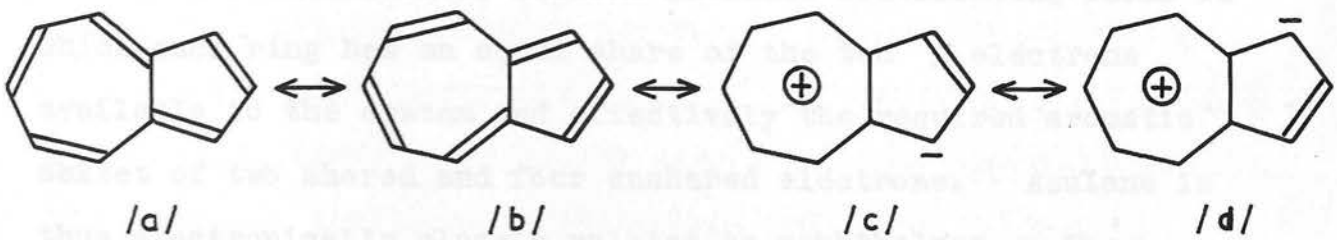
Craig (J., 1951, 3175) has recently suggested a classification based on symmetry as a criterion of aromaticity; it only applies

to molecules which have one or more twofold axes passing through at least two of the π-centres. The possession of an unsymmetrical electronic ground state is taken as indicating a type of π-electron interaction which is unfavourable to aromatic character and which does not lead to big resonance energies; the valence-bond theory enables the ground state symmetry to be correctly predicted. Aromatic compounds (possessing the required symmetry for the application of this criterion) were found to have totally symmetrical ground states. On the other hand, unsymmetrical ground states were found for a large number of molecules which are as yet unknown and proved difficult to synthesise. Examples of this type of molecule, for which the name "pseudoaromatic" has been suggested, are pentalene and heptalene; additionally the class includes all monocyclic molecules of the Hückel $4n$ type starting with cyclobutadiene. Craig's symmetry criterion cannot be applied to molecules not possessing the required symmetry, e.g., phenanthrene or chrysene.

The fact that the cyclopentadiene ring is most stable in the form of the negative ion while cycloheptatriene forms a stable positive ion leads to the conclusion that the most stable of the ring systems XIII - XV will be XIV; it corresponds to azulene which was shown previously to possess distinctly aromatic character.

The evidence for the stability of the cyclopentadienyl anion and the cycloheptatrienylium cation also supports the view that

the resonance hybrid of azulene has contributions from forms in which an electron is transferred from the seven- to the five-membered ring, giving six π electrons in each (Stafford and Reid, Chem. and Ind., 1954, 277; Galloway, Reid and Stafford, ibid., 1954, 724; Reid, Stafford and Ward, J., 1955, 1193). The conclusion was reached that azulene XVII can best be represented, in both ground and reacting states, as a resonance hybrid of two classical, covalent structures (a) and (b) and fourteen betaine forms included in the collective structures (c) and (d).

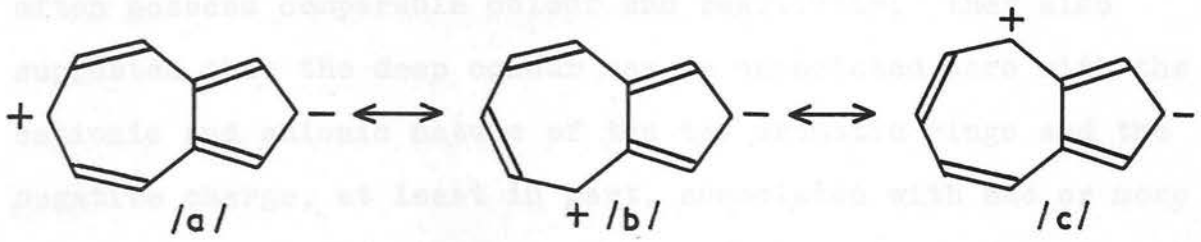


/a/ /b/ /c/ /d/

XVII

Anderson, Nelson and Tazuma (J.A.C.S., 1953, 75, 4980) arrived at the same result but from consideration of the aromaticity of the system shown by its substitution reactions and they represented the reacting structure of azulene by formulas XVII (c) and (d). In 1952 Treibs (Ann., 1952, 576, 110) postulated contribution from forms XVIII (a), (b) and (c), but being quinonoid in nature,

they can be expected to be least important.



/a/ + /b/ /c/

XVIII

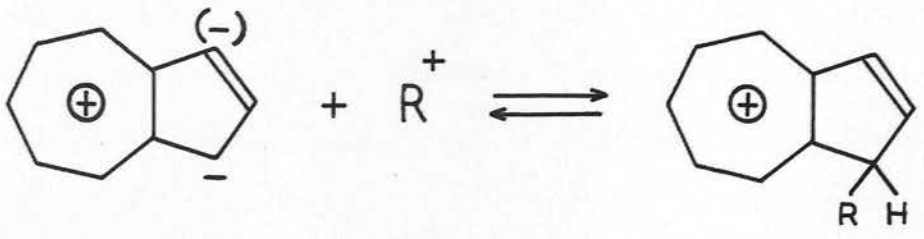
The significant betaine forms are only those included in the collective structures XVII (c) and (d). These fourteen ionic forms, together with the two Kekulé-type structures, give a fair representation of the azulene molecule.

This formulation of azulene includes contributing forms in which each ring has an equal share of the ten π electrons available to the system and effectively the required aromatic sextet of two shared and four unshared electrons. Azulene is thus electronically closely related to naphthalene. The properties are, however, very different for in azulene contribution of the dipolar forms shows that electron transfer has occurred and although the molecule as a whole is electrically neutral, there is a partial separation of charge. On this basis azulene is an aromatic system with the unusual features that two equivalent positions in the five-membered ring possess a high electron density, balanced by an attenuation of the π-electronic density in the seven-membered ring.

This representation of azulene interprets its reactions and includes it within the class of anhydro-bases, which Galloway,

Reid and Stafford (Chem. and Ind., 1954, 277, 724) have indicated often possess comparable colour and reactivity; they also suggested that the deep colour may be associated here with the cationic and anionic nature of the two aromatic rings and the negative charge, at least in part, associated with one or more carbon atoms. This interpretation of the colour of azulene is, however, at variance with views expressed by Heilbronner ("Azulenes" in "Non-benzenoid Aromatic Compounds", edited by Ginsburg), who considers that certain deductions made from the resonance formulation of azulene are not necessarily warranted by this model, as for example, the explanation of colour. He points out that the longwave absorption in azulene can be taken as, "... primarily the consequence of its particular type of topology, as exemplified by the simple valence bond model based on the apolar limiting structures ..." XVII (a) and (b).

The properties of azulene manifest the tendency of the rings to achieve an ultimate state in which each contains six π-electrons. One typical property is the ready polarisibility of the system; in appropriate circumstances an electron pair may be developed on either $C_{(1)}$ or $C_{(3)}$ and shared with an electrophilic group.



XIX

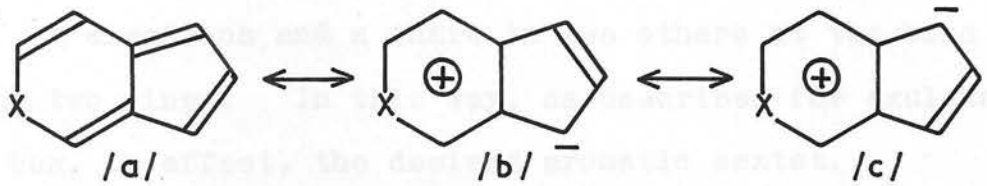
The basicity of azulene manifests both this polarisibility and the stability of the polarised state once the electrons have been shared, i.e. it reflects the stability of the cyclopentadieno-cycloheptatrienylium ion XIX, to which the name of azulenium cation has been given by Plattner, Heilbronner and Weber (Helv. Chim.Acta, 1952, 35, 1036).

The positions of electrophilic and nucleophilic substitution in azulene can be explained by considering accumulations of charge in the resonance hybrid.

The terms heterocyclic analogue of azulene or pseudoazulene are used here throughout to denote compounds of type II or III, obtained by replacement of the -CH=CH- grouping in the seven-membered ring of azulene by a hetero-atom. The above terms do not refer here to, e.g., azaazulenes, where a nitrogen atom replaces a -CH- grouping (one carbon atom) in the five- or seven-membered azulene ring.

Like azulene, its heterocyclic analogues or pseudoazulenes II and III and their derivatives show deep colour, basicity, and substitution. They are iso-electronic with and retain the aromatic character of the parent hydrocarbon and can also be represented as resonance hybrids of covalent and dipolar forms.

Thus, for example, III; X = NR, S, or O may be represented as a resonance hybrid of the following canonical forms:



XX

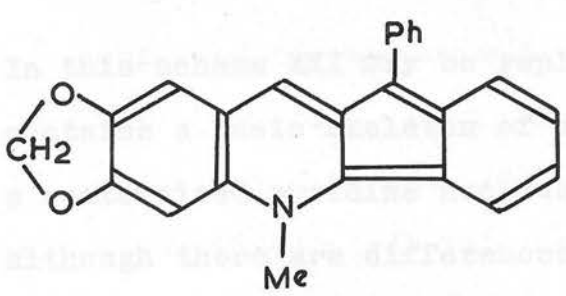
In the sulphur compounds, however, contribution may also be expected from covalent forms in which the valence shell of sulphur is expanded to accommodate ten electrons. This will be discussed later, when consideration will be given to the influence of different hetero-atoms on the absorption spectrum and basicity of analogous pseudoazulenes.

This representation of pseudoazulene (XX) may be compared with the parent compound as formulated in XVII. Here XX (a) is uniquely covalent and comparable to the two classical azulene forms XVII (a) and (b). The dipolar forms XX (b) and (c) are also comparable to the corresponding azulene structures XVII (c) and (d), for they represent a fusion of the five-membered anion and the

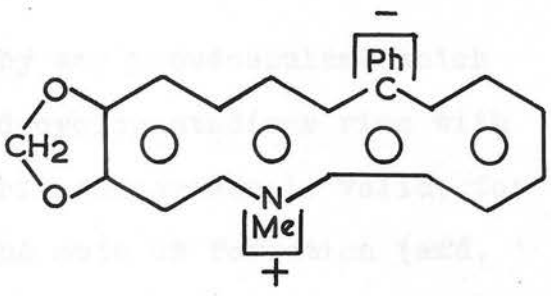
six-membered hetero-ring cation, which both constitute stable aromatic species. Electronically there is little difference between azulene and its heterocyclic analogues. The replacement of the -CH=CH- grouping in the seven-membered ring of azulene by a hetero-atom, provided with a lone pair of electrons, does not alter the total number of π electrons available to the system, which remains ten. As in azulene there are canonical forms contributing to the resonance hybrid in which each ring has four π electrons and a share in two others at the bond of fusion of the two rings. In this way, as described for azulene, each ring has, in effect, the desired aromatic sextet.

This formulation of the pseudoazulenes interprets their properties and together with the azulenes includes them in the class of anhydro-bases.

The unsubstituted N-methyl-1-pyrindine (II; X = NCH_3) has not yet been prepared but its complex derivatives have been known for over thirty years since Armit and Robinson (J., 1922, 121, 857; ibid., 1925, 127, 1604) prepared the indenoquinolines, e.g., XXI, in order to show that aromatic character may be associated with a five-membered carbon ring ("the pentamethine nucleus") in a suitable combination. They effectively represented XXI as a resonance hybrid of the structures (a) and (b), although their paper appeared before the theory of resonance was proposed.



/a/

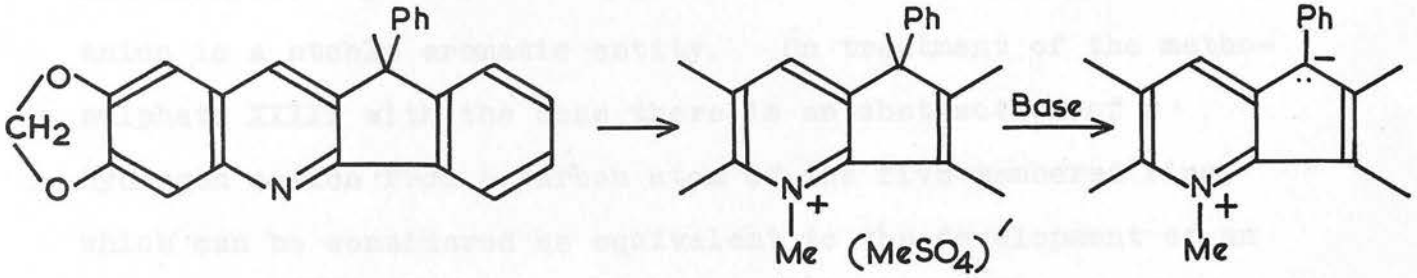


/b/

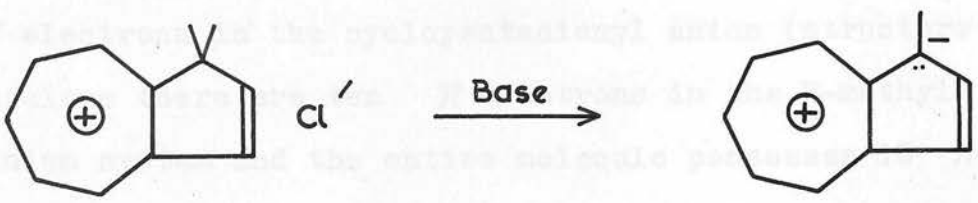
XXI

They stated that: (a) "... is not stable because the right-hand benzene ring is not aromatic ..." and (b) "... is not stable because it is a dipole; the tendencies to aromatic sextet formation and to neutralisation of the charges work in opposite directions and must reach some compromise".

In the formation of XXI from 7,8-methylenedioxy-11-phenyl-indenoquinoline XXII a direct comparison can be made with azulene as formulated in XXV.



XXII XXIII XXIV ≡ XXI/b/



XXV

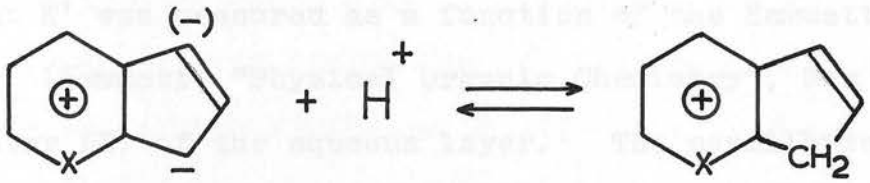
In this scheme XXI may be replaced by any pseudoazulene which contains a basic skeleton of a fused cyclopentadiene ring with a quaternised pyridine nucleus. This comparison is valid, for although there are differences in the mode of formation (and, for example, salts of azulene are only formed in strong acid), they are not fundamental and are only matters of degree.

The derivation of the electronic state of XXI further illustrates the close structural relationship between azulene and its heterocyclic analogues. The nitrogen atom of the pyridine ring, (as in XXII), has a pair of unshared electrons and in quaternisation there is an electrophilic attack by methyl cation on this electron pair. As a result both electrons take part in a C-N covalent bond, with the nitrogen atom now sharing its lone pair of electrons and thus possessing a positive charge (XXIII). In monocyclic systems it has been seen that the cyclopentadienyl anion is a stable aromatic entity. On treatment of the methosulphate XXIII with the base there is an abstraction of a hydrogen cation from a carbon atom of the five-membered ring, which can be considered as equivalent to the development of an electron pair on that atom. This electron pair then joins the two electrons from the double bond and uniting with the pyridine sextet is absorbed into the molecular orbital giving a total of six π electrons in the cyclopentadienyl anion (structure XXIV). As in azulene there are ten π electrons in the N-methyl pyrindinium system and the entire molecule possesses 18 π electrons

available for the aromatic sextet formation, as indicated by XXI (b).

Armit and Robinson referred to XXI as an anhydronium base and they proposed that this name should be reserved only for those compounds which are recognizably intermediate between neutral and fully polarised forms. As has already been indicated, all pseudoazulenes can be regarded as anhydro-bases and since they are electronically analogous with azulenes, the latter are also included in this class of compounds (Galloway, Reid and Stafford, Chem. and Ind., 1954, 724).

The basicity of pseudoazulenes follows from the established structure and reflects the equilibrium:



II XXVI

Like the parent hydrocarbon, the pseudoazulene, e.g., II; X = NR, S or O, may be considered as the conjugate base of the Brønsted acid XXVI, which is the heterocyclic analogue of the azulenium cation XIX; R = H. The basicity shows how readily an electron pair can be localised and shared with the hydrogen ion and also the stability of the polarised state once the electrons have been shared, i.e. it reflects the stability of the corresponding cation XXVI.

Evaluation of basicity.

The basicities of a large number of azulenes have been characterised by Plattner, Heilbronner and Weber (Helv.Chim.Acta, 1949, 32, 574) through the distribution coefficients K' obtained for a system composed of an aqueous acid and an inert organic solvent,

$$K' = \frac{\text{Concentration of azulene in the inert solvent}}{\text{Concentration of azulene in the aqueous acid.}}$$

The solvent systems used were the four possible combinations of aqueous sulphuric acid and phosphoric acid together with toluene or petroleum ether as the organic solvent. The distribution coefficient K' was measured as a function of the Hammett acidity function H_o (Hammett, "Physical Organic Chemistry", New York, 1940, Chapter IX) of the aqueous layer. The equilibrium $I + H^+ = XIX$; R=H is truly reversible and the logarithm of K' was observed to depend linearly upon the value H_o of the aqueous layer. To determine the basicity of the azulene, Plattner, Heilbronner and Weber have chosen the H_o value for which the coefficient K' becomes unity, H_o (K' = 1), and published tables of such values for the above-mentioned systems (Helv.Chim.Acta, 1949, 32, 574, 2464; Plattner et al., ibid., 1950, 33, 1912). Aitken and Reid (J., 1956, 3487) applied the same procedure to indeno[2,1-a]perinaphthene which represents a new class of basic hydrocarbons of which the simplest member is the still unknown

cyclopenta[a]perinaphthene. The value of $H_o(K'=1)$ found for this compound placed it alongside the azulenes in order of basicity.

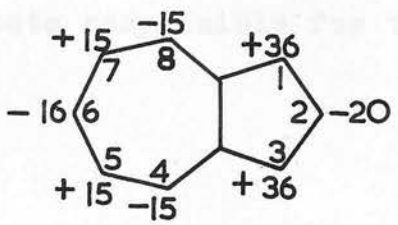
The basicities of a large number of pseudoazulenes were determined also using Plattner's procedure. The pseudoazulene was partitioned between benzene and sulphuric acid of different strengths and, as in the parent hydrocarbons, a linear relationship was observed between $\log_{10} K'$ and H_o. The basicity was found to vary considerably with the hetero-atom and to a lesser extent with the nature and number of the substituents. The pseudoazulenes examined could in general be placed alongside azulenes in order of basicity, except for the nitrogen compounds which were particularly basic. Such comparisons however are <u>not</u> strictly quantitative since $H_o(K'=1)$ constants may be taken as measures of the relative basicities of azulenes only if it is assumed that the true distribution coefficient of the <u>free hydrocarbon</u> between the organic solvent and the aqueous layer is the same for the azulenes to be compared - and the same argument holds equally well for the pseudoazulenes. While the above assumption may well hold for certain very closely related systems, it would not be correct if, e.g., azulene was quantitatively compared with its heterocyclic analogues or with higher condensed azulenes, such as the benzazulenes.

Absorption Spectra

Many derivatives of azulene are now known and attempts have been made to correlate their spectra. Azulenes show a broad absorption band in the visible and two main bands in the ultraviolet region of the spectrum.

The ultraviolet spectra of alkyl azulenes were examined by Plattner and Heilbronner (Helv.Chim.Acta, 1948, 31, 804) who found that, as in alkylated benzenoid compounds, all five monomethyl azulenes absorbed at longer wavelengths than the parent substance. Multiple substitution of alkyl groups tends to obliterate part of the fine structure of the bands, but even substitution by strongly polar groups does not change the typical aspect of the azulene ultraviolet spectrum.

The additivity of spectral shifts in the visible region, caused by alkyl groups on the different positions of the azulene ring, was first noted by Plattner and has been known as Plattner's Rules (Helv.Chim.Acta, 1941, 24, 283E). The displacement relative to azulene is hypsochromic or bathochromic, dependent on the position of substitution as shown in XXVII, but comparatively independent of the size of the alkyl substituent (Plattner and Fürst, Helv.Chim.Acta, 1945, 28, 1636). If the alkyl groups

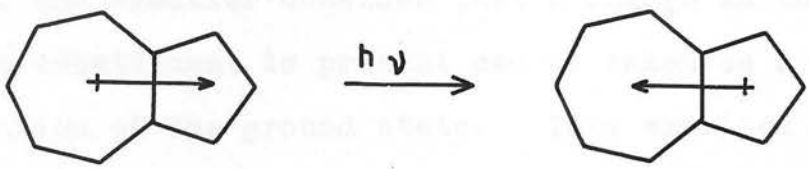


XXVII

(electron donating) are replaced by electron attracting groups (e.g. carbethoxy group), the displacements are reversed. Apolar hydrocarbons are preferable as solvents, because more polar solvents tend to obliterate the very characteristic fine structure of the bands. Furthermore, slight hypsochromic shifts are observed if a solvent of low dielectric constant (e.g. cyclohexane) is replaced by a solvent of higher dielectric constant (e.g. ethanol).

Plattner's Rules have been extended by Anderson and co-workers (e.g., J.Org.Chem., 1957, 22, 1193; J.A.C.S., 1957, 79, 6511; ibid., 1953, 75, 4980) to 1- and 1,3- substituted azulenes containing a variety of groups other than alkyl. Cowles (J.A.C.S., 1957, 79, 1093) has done a more quantitative study with respect to certain of these groups. The conclusion was reached that a substituent (on the 1-position) which was o- or p- directing in benzene would cause a bathochromic displacement in the absorption maximum but if a substituent possessed m- directing power a hypsochromic shift would result (Anderson and Steckler, J.A.C.S., 1959, 81, 4941).

The explanation which was advanced to account for the substituent effects of different types of groups is based on the reversion of the azulene dipole on passing from the ground state to the excited state responsible for the absorption band in the visible region.



Ground state Excited state

The orientation of the dipole in the ground state was originally proposed by Wheland and Mann (J.Chem.Phys., 1949, 17, 264) who obtained the calculated value for the dipole moment as 1-2 D. and the experimental value as 1.00±0.05 D. Kurita and Kubo (J.A.C.S., 1957, 79, 5460) and Anderson and Steckler (loc.cit.) obtained dipole moments of a number of azulene derivatives and confirmed the orientation of the dipole. Knowledge about the excited state of the azulene molecule responsible for the visible band was provided by the calculations of Pariser (J.Chem.Phys., 1956, 25, 1112) who gave a value of -1.36 D. for the required excited state.

The change in the orientation of the dipole indicates a demand by the excited azulene nucleus for electrons from substituents on the five-membered ring and a group possessing an inherent ability for donating electrons would stabilise the excited state. If the substituent stabilised the ground state to a lesser extent, a decrease in excitation energy would result and a bathochromic shift in the maximum absorption would be observed.

Anderson and Steckler consider that a change in the dipole moment when a substituent is present can be taken as a measure of (de)stabilisation of the ground state. They examined different substituents, causing bathochromic or hypsochromic displacements, and found that both types of groups increased the dipole moment and therefore stabilised the ground state. If the ground state was thus stabilised and the excited state remained unaltered, then an increase in excitation energy would result and hypsochromic displacement would be observed. Consequently, an absorption shift not corresponding to the stabilisation of the ground state would be due to the effect of the substituent on the excited state.

The nitro group (position 1) is able to stabilise markedly the ground state through both resonance and inductive mechanism but has little or no ability to stabilise the excited state and an increase in the excitation energy results, causing a hypsochromic shift. In the case of the alkyl groups, stabilisation of the excited state through an inductive (and/or hyperconjugative) mechanism exceeds any small change in the ground state, while phenyl groups are able to stabilise both states (by resonance and also by induction), but the effect is greater on the excited state. Thus both alkyl and phenyl groups (positions 1, 3) cause bathochromic displacements.

Phenyl substitution, however, presents different problems than those encountered in alkyl azulenes, for it deals with substituents which are able to conjugate to a very considerable extent with the azulene nucleus. Molecular orbital theory predicts bathochromic shifts for all phenyl-azulenes, with the largest shifts for positions 1, 4 and 6 (Pullman et al., J.chim.phys., 1953, 50, 69). The values for the wavelengths of the maximum absorption (the principal maximum) in the visible region ($\lambda_{max.}$) and the shifts from the maximum of azulene ($\Delta\lambda_{max.}$) of the five isomeric phenylazulenes are collected in Table I; it will be seen that, with the exception of 2-phenyl-azulene, which shows a barely significant hypsochromic shift, they all exhibit bathochromic shifts of their long wave absorptions.

TABLE I.

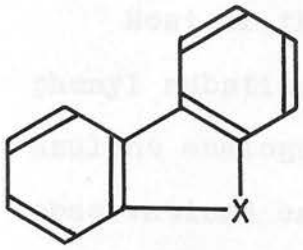
(All spectra were determined in an apolar hydrocarbon solution.)

Compound	λ max. (mμ)	$\Delta\lambda$ max. (mμ)	Refs.
Azulene	580		1
1-Phenylazulene	606	+ 26	2
2-Phenylazulene	578	- 2	2
4-Phenylazulene	583	+ 3	3
5-Phenylazulene	593	+ 13	4
6-Phenylazulene	590	+ 10	5

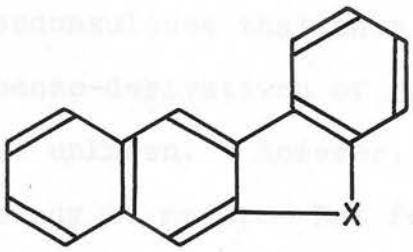
1. Kloster-Jensen, Kovats, Eschenmoser and Heilbronner, Helv.Chim.Acta, 1956, 39, 1051.
2. Plattner et al., Helv.Chim.Acta, 1950, 33, 1910; ibid., 1946, 29, 1604.
3. Hafner and Weldes, Ann., 1957, 606, 90.
4. Pommer; $\lambda_{max.}$ given by Heilbronner, "Azulenes" in "Non-benzenoid Aromatic Compounds".
5. Prelog and Polyak, Helv.Chim.Acta, 1957, 40, 816.

The situation in phenylazulenes is complicated, however, by the presence of steric inhibition of the coplanarity of the benzene nucleus with the azulene system and because the polarity of the carbon-carbon bond joining the phenyl groups to the azulene nucleus is not necessarily the same if the phenyl groups are attached to the five-membered ring or to the seven-membered one. It is predicted that 2-, 5- and 6-phenylazulenes will show no steric effects in their spectroscopic behaviour, whereas 1- and especially 4-phenylazulenes should exhibit a considerable lack of coplanarity due to "overlap" of hydrogen "interference radii" (Braude, Experientia, 1955, 11, 457; Heilbronner, "Azulenes").

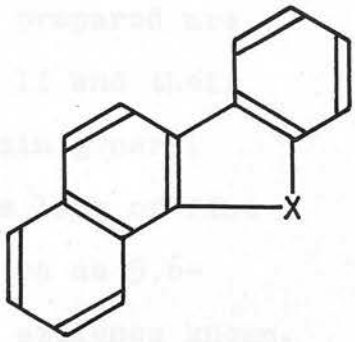
The absorption spectra of polycyclic benzenoid hydrocarbons and those of the corresponding furans, thiophenes and pyrroles have been studied by Badger and Christie (J., 1956, 3438) and found to be fundamentally similar. Three main regions of absorption could generally be resolved. In the heterocyclic compounds absorption was normally shifted to shorter wavelengths and group III bands (in the near ultraviolet region) had much higher extinction coefficients than those given by the corresponding hydrocarbons.



XXVIII



XXIX



XXX

It is also of interest to note that in the higher heterocyclic systems, e.g., XXVIII, XXIX, and XXX, the order of decreasing wavelength of maximum absorption in the group III bands was -

$$X = NH > S > O$$

A similar general comparison of azulenes with the corresponding heterocyclic systems II and III and their derivatives cannot at present be absolute, because there are so few pseudoazulenes known which can be compared with the analogously substituted hydrocarbons. The available evidence, which will be discussed later, indicates that, as in benzenoid compounds, introduction of a hetero-atom causes a hypsochromic shift, (but this time in the visible absorption), and that the unsubstituted analogues of azulene resemble the parent in showing a fine structure of the visible absorption band (Anderson et al., J.A.C.S., 1959, 81, 1255).

Most of the pseudoazuleues that have been prepared are phenyl substituted benzo-derivatives of system II and their azulene analogues are unknown. However, certain general observations can already be made. But for the lack of fine structure they show the same three-banded spectra as 5,6- and 1,2-benzazulenes, the most closely related azulenes known. Like azulenes, the heterocyclic analogues show a band of medium strength in the visible spectrum, which disappears in acid solution, and two intense bands in the ultraviolet. The relative displacements of the visible absorption band generally conform with expectations for azulene derivatives; exceptions were encountered in highly substituted compounds carrying a large number of phenyl groups, where molecular overcrowding prevents coplanarity of certain of these groups with the rest of the molecule.

The effect of the steric inhibition of coplanarity on the visible absorption of phenyl substituted pseudoazulenes will be discussed later more fully; consideration will also be given to the absorption spectra of analogous pseudoazulenes differing only in the nature of the hetero-atom.

Objects of research

1. Synthesis and study of the sulphur analogues of azulene.

2. Examination of the influence of different hetero-atoms on the absorption spectrum, basicity, and stability of analogous nitrogen, sulphur, and oxygen pseudoazulenes.

3. Study of the effect of substituents on the visible absorption spectrum of pseudoazulenes.

4. Synthesis and study of heterocyclic systems (the pseudo-aza-azulenes) obtained by replacement of a CH group by an atom of nitrogen in the six-numbered hetero-ring of pseudo-azulenes.

Nomenclature and Numbering

The nomenclature and numbering in the heterocyclic analogues of azulene has not yet been settled and several systems are in current use. Those adopted here are generally in agreement with the recent usage in the publications of the Chemical Society.

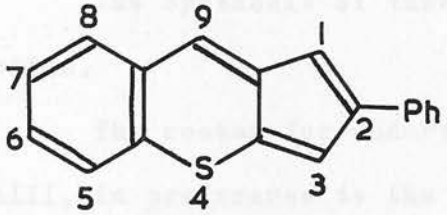
System II; X = NH is thus named "1 H-cyclopenta [b] pyridine", while the American authors prefer "1-pyrindine" and in the German journals the name "1-azalene" has been suggested. By analogy, II; X = O and X = S correspond to cyclopenta [b] pyran and cyclopenta [b]-thiapyran, respectively.

The numbering adopted here is in accordance with the I.U.P.A.C. Rules (Handbook for Chemical Society Authors, 1960).

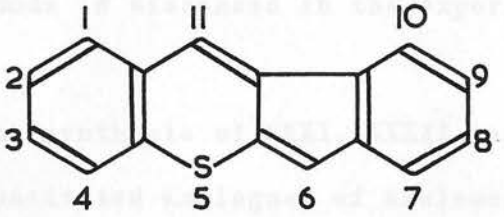
Discussion

When this research was undertaken (1957), sulphur pseudoazulenes were unknown. In the same year Mayer (Angew. Chem. 1957, 69, 481) claimed to have synthesised the parent sulphur compound II ; X = S and its 1,2-benzoderivative from 2-carbethoxy-cyclopentan-1-one, but he gave no experimental details (and since then no further information appears to have been published). It therefore seemed desirable to obtain a definite experimental proof that a - CH = CH - grouping in the seven-membered ring of azulene could be replaced by a sulphur atom, while still retaining those properties peculiar to the azulenic system.

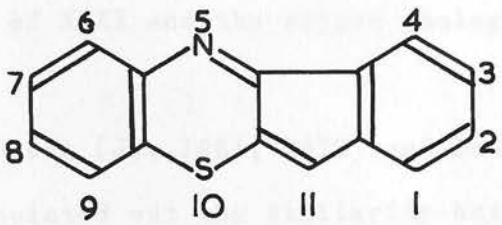
Two sulphur pseudoazulenes, 2-phenylbenzo[b]cyclopenta[e]-thiapyran XXXI, and benzo[b]indeno[1,2-e]thiapyran XXXII, and one sulphur pseudoaza-azulene, benzo[b]indeno-[1,2-e] -[1,4]- thiazine XXXIII have been synthesised.



XXXI



XXXII



XXXIII

They are, respectively, the heterocyclic analogues of the still unknown, 2-phenyl-5, 6-benzazulene, 2,3,5,6-dibenzazulene, and 4-aza-2,3,5,6-dibenzazulene.

All the three sulphur compounds were obtained as intensely red or mauve, beautifully crystalline solids. Unlike their nitrogen analogues, they were remarkably stable and could be kept apparently indefinitely in the solid state. Solutions kept in darkness and in the absence of air remained unchanged for several months, but on exposure to atmospheric oxidation or strong sunlight they decomposed much more rapidly.

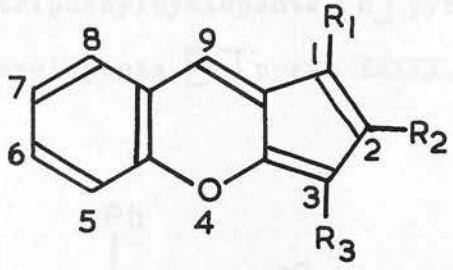
Sulphur pseudoazulenes show a three-banded spectral system similar to that in azulenes. With mineral acids they form deep yellow or green salts which, in solution exhibit an intense fluorescence. Unlike the azulenes and their nitrogen analogues the sulphur compounds do not form molecular complexes with 1,3,5-trinitrobenzene or 2,4,7-trinitrofluorenone.

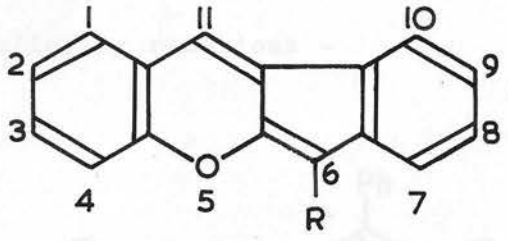
The synthesis of these compounds is discussed in the experimental section.

The reason for undertaking the synthesis of XXXI, XXXII, and XXXIII, in preference to the less substituted analogues of azulene, was connected with the second object of this research, (to compare analogous nitrogen, sulphur and oxygen pseudoazulenes) since the nitrogen and the oxygen analogues of XXXI and the oxygen analogue of XXXII were already known.

In 1951 Brown (J., 1951, 2670) and Dauben and Ringold (J.A.C.S., 1951, 73, 876), pointed out the similarity between tropone and γ-pyrone.

Mayer (Chem. Ber., 1957, 90, 2369) has extended this and shown that 3-hydroxy α- and γ-pyrones could be regarded as pseudotropolones. At the same time Boyd (Chem. and Ind., 1957, 1244; J., 1958, 1978) reported the synthesis of highly substituted oxygen pseudoazulenes, 2-phenylbenzo [b] cyclopenta [e] -pyran XXXIV and benzo [b] indeno - [1,2-e] pyran XXXV, which were the first derivatives of system II; X = O.





XXXIV; $R_1 = R_3 = H$, $R_2 = Ph$

XXXVI; $R_1 = R_2 = Ph$, $R_3 = H$

XXXVII; $R_1 = H$; $R_2 = R_3 = Ph$

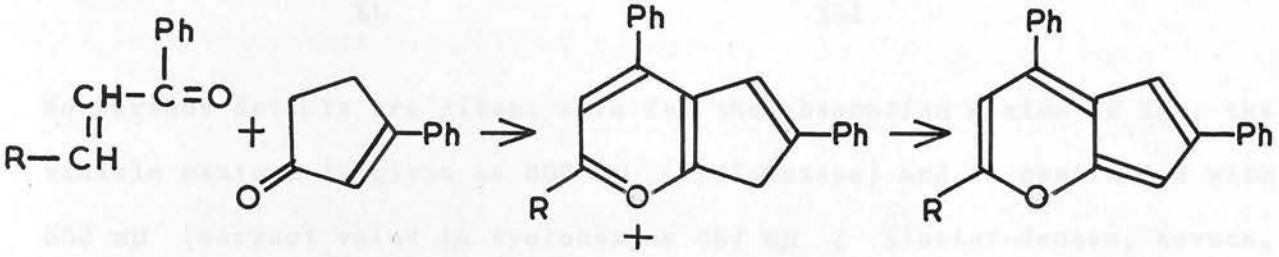
XXXV; R = H

Compounds XXXIV and XXXV, like their sulphur analogues XXXI and XXXII, respectively, are stable, reddish coloured, crystalline solids. They behave as anhydro-bases of their respective pyrylium perchlorates, into which they are converted by treatment with perchloric acid and from which they can be obtained by the action of alkali or water. The pyrans dissolve in concentrated hydrochloric acid giving a yellow solution with a bluish fluorescence and are regenerated on dilution.

The synthesis of XXXIV and XXXV was repeated and the 2,3-diphenyl

derivative of XXXIV prepared (XXXVII); the synthesis of the 1,2-diphenyl derivative XXXVI has also been reported (Los and Stafford, J. 1959, 1680). In their colour, spectra and basicity the oxygen pseudoazulenes resemble their sulphur analogues and the azulenes; like the former they do not form molecular complexes with 1,3,5-trinitrobenzene.

Boyd has also prepared two other oxygen pseudoazulenes, 2,4,6-triphenylcyclopenta [b] pyran XXXVIII and 2-tert. butyl-4,6-diphenyl-cyclopenta [b] pyran XXXIX, by the following reactions -



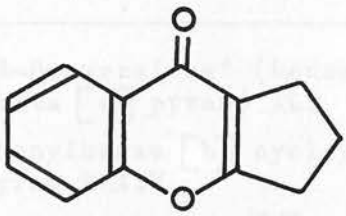
XXXVIII; R = Ph

XXXIX; R = Bu^t

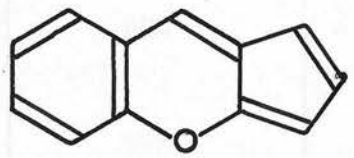
The cyclopentapyrans XXXVIII and XXXIX closely resemble the benzo-derivatives. Solutions of their salts exhibit an intense green fluorescence, typical of pyrylium salts. It is significant that ammonia converts the perchlorates into the corresponding cyclopentapyrans and not into derivatives of pyridine, a reaction characteristic of pyrylium salts. Compounds XXXVIII and XXXIX have similar absorption spectra; substitution of the phenyl group for the tert. butyl group produces the expected

bathochronic shift.

Mayer and Weise (Naturwiss., 1958, 45, 313) claim to have prepared unsubstituted benzo [b] cyclopenta [e] pyran XLI by condensation of phenol with 2-carbethoxy-cyclopentanone to the chromone XL, which gave the required product by reduction of the carbonyl to the methylene group, followed by dehydrogenation with chloranil.



XL



XLI

No further details are given, save for the absorption maxima of XLI; the visible maximum is given as 506 mμ (cyclohexane) and is contrasted with 552 mμ (correct value in cyclohexane 557 mμ ; Kloster-Jensen, Kovats, Eschenmoser and Heilbronner, Helv. Chim. Acta, 1956, 39, 1051) for the parent 5,6-benzazulene. This represents a hypsochromic shift of 51 mμ on replacement of a -CH = CH- grouping of the seven-membered ring of the benzazulene by an atom of oxygen. By analogy with the azulenes Mayer and Weise proposed the name "oxalenes" for the oxygen pseudoazulenes derived from system II; X = O. The values for the visible absorption maxima of XLI ("2,3-benzoxalene") and its known derivatives are collected in Table II, together with the relevant data for the azulenes (cf. Table I).

TABLE II

Compound	λ max.* (Cyclohexane)	λ max. (ethanol)
Azulene	580	577
1-Phenylazulene	606	
2-Phenylazulene	578	
5,6-Benzazulene	557	552
"2,3-Benzoxalene" (benzo [b] cyclopenta [e] pyran) XLI	506	
2-Phenylbenzo [b] cyclopenta [e]-pyran XXXIV		470
1,2-Diphenylbenzo [b] cyclopenta [e]-pyran XXXVI		512
2,3-Diphenylbenzo [b]cyclopenta [e]-pyran XXXVII		510

* mμ

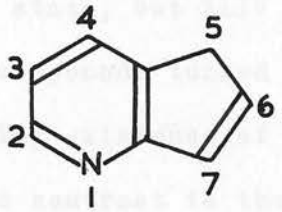
Phenyl substituted 5,6-benzazulenes are unknown and therefore the displacements in the visible absorption obtained on substitution in the benzo [b] cyclopenta [e] pyran nucleus can only be compared with analogous displacements in azulene. Introduction of a phenyl group into the 2-position of azulene produces only a very small hypsochromic shift (2 mμ). In the benzocyclopentapyran series the spectral evidence of Mayer and Weise indicates that a 2-phenyl substituent causes a hypsochromic shift of 36 mμ . This would represent a considerable difference in spectral behaviour between azulene and the oxygen analogue of the benzazulene (XLI.) However, this result which only follows from the work of Mayer and Weise, should be contrasted with the values quoted for the absorption maxima of other

compounds in the benzocyclopentapyran series (XXXIV, XXXVI, and XXXVII), for they indicate a much closer correspondence with shifts observed in azulene derivatives. Thus a bathochromic shift obtained on introduction of a phenyl group into the 1- or 3-position of 2-phenylbenzo [b] cyclopenta [e] pyran XXXIV (40–42 mμ) can be compared with a shift of + 26 mμ shown by 1-phenylazulene. Even closer correspondence with azulene is observed in the analogous nitrogen pseudoazulenes where the nitrogen analogue of 1,2-diphenylbenzo [b] cyclopenta [e] pyran XXXVI shows a bathochromic shift of 22 mμ from the 2-phenyl derivative (Los and Stafford, J. 1959, 1680).

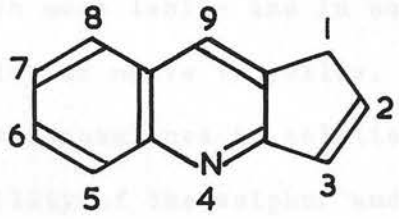
In the absence of other data no definite conclusions can be drawn but even allowing for the slight hypsochromic shift observed on replacement of a solvent of low dielectric constant (cyclohexane) by a solvent of higher dielectric constant (ethanol), the value for the visible absorption maximum quoted by Mayer and Weise for XLI appears excessively high and requires a definite experimental proof before it can be accepted.

While the interest in the oxygen and sulphur analogues of azulene is only of a very recent date, complex derivatives of the system II; X = NR have been known since 1922 - 1925 when Armit and Robinson (J. 1922, 121, 827; 1925, 127, 1604) synthesised the deeply coloured indenoquinolines e.g., XXI, to prove that aromatic character may be associated with a five-membered ring. No further work was published in this field until, in recent years, renewed interest in such systems was stimulated by their structural relationship to azulene. Los and Stafford (J., 1959, 1680; and with Saxena, Proc. Chem. Soc., 1957, 352) made several attempts

to prepare simple nitrogen analogues but they encountered considerable difficulties in the synthesis of the hitherto unknown 5 H-cyclopenta [b] pyridine (β -pyrindine) XLII and 1-H-cyclopenta [b] quinoline (β-quinindine) XLIII compounds and were able to obtain the desired system only in the form of the more complex derivatives.

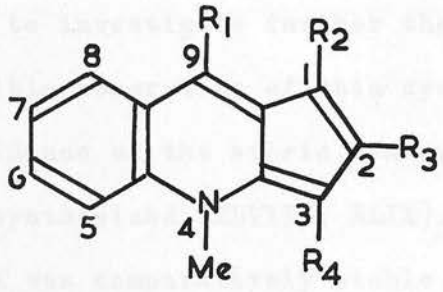


XLII



XLIII

Compounds XLII and XLIII are represented here as possessing a 6,7 and a 2,3 double bond respectively, but as in substituted indenes, there is a possibility of a bond migration to positions 5,6 and 1,2, according to which is more stable.



XLIV; $R_1 = R_2 = R_4 = H$, $R_3 = Ph$

XLV; $R_1 = COOMe$, $R_2 = R_4 = H$, $R_3 = Ph$

XLVI; $R_1 = R_4 = H$, $R_2 = R_3 = Ph$

XLVII; $R_1 = COOMe$, $R_2 = R_3 = Ph$, $R_4 = H$

XLVIII; $R_1 = R_2 = H$, $R_3 = R_4 = Ph$

XLIX; $R_1 = COOMe$, $R_2 = H$, $R_3 = R_4 = Ph$

L; $R_1 = Me$, $R_2 = R_3 = H$, $R_4 = Ph$

Los and Stafford prepared four derivatives of cyclopenta [b] quinoline, XLIV - XLVII. All compounds were intensely blue or mauve and except for XLVII, could only be obtained in the crystalline state as their 1,3,5-trinitrobenzene complexes. Compound XLVII, stabilised by a carbomethoxy and two phenyl groups, appeared indefinitely stable in the solid state, but XLIV - XLVI were much more labile and in solution all four compounds turned rapidly from blue or mauve to yellow. The fleeting existence of the nitrogen pseudoazulenes in solution is in marked contrast to the relative stability of the sulphur and oxygen analogues. With dilute acid, the nitrogen compounds formed yellow salts which fluoresced intensely blue in solution. The salts reverted in part to the blue or mauve state when suspended in water or ethanol.

Spectral data indicated molecular overcrowding in XLVII which prevents the coplanarity of the 1-phenyl group with the rest of the molecule. In order to investigate further the effect of phenyl substituents on the visible absorption of this system and particularly to obtain additional evidence of the steric hinderance, two new compounds of this series were synthesised (XLVIII, XLIX). The deep blue carbomethoxy compound XLIX was comparatively stable and even in solution remained unaltered for some weeks if kept in darkness and in the absence of air. The 9-carbomethoxy group exerts a stabilising influence and the mauve decarboxylated compound XLVIII decomposed much more rapidly.

The values for the visible absorption maxima (λ max.) of compounds XLIV - XLIX, and for the shifts caused by phenyl substituents in the

1- and 3-positions of 2-phenyl-4-methylcyclopenta [b] quinoline XLIV and of its 9-carbomethoxy derivative XLV ($\Delta\lambda$ max.) are collected in Table III.

TABLE III

(Solvent : ethanol)

Compound *	λ max. (mμ)	$\Delta\lambda$ max. (mμ)
2-phenyl-4-methylcyclopenta [b]-quinoline XLIV	532	
1,2-diphenyl derivative XLVI	554	22
2,3-diphenyl derivative XLVIII	533	1 (approx. 0)
2-phenyl-4-methyl-9-carbomethoxy-cyclopenta [b] quinoline XLV	574	
1,2-diphenyl derivative XLVII	574	0
2,3-diphenyl derivative XLIX	574	0

* T.N.B.

It has been seen that in the analogous oxygen series, 1,2- and 2,3-diphenylbenzo [b] cyclopenta [e] pyrans XXXVI and XXXVII show approximately equal bathochromic shifts from the 2-phenyl derivative XXXIV (40-42 mμ). The nitrogen analogue of XXXIV, 2-phenyl-4-methyl-cyclopenta [b] quinoline XLIV shows maximum absorption at 532 mμ and the introduction of the second phenyl group into position 1 of the pseudoazulene nucleus (XLVI) causes the expected bathochromic shift (22 mμ). If, however, the second phenyl substituent occupies position 3 (XLVIII), there is no bathochromic displacement and the wavelength of

maximum absorption remains unaltered (533 mμ). Similarly the visible absorption of XLV, XLVII, and XLIX is also identical. Here the presence of the phenyl groups in both 1 and 3 positions does not affect the absorption maxima.

This spectral behaviour can only be explained by the molecular overcrowding which would prevent the coplanarity of certain phenyl groups with the rest of the molecule. Thus in compound XLVII the coplanarity of the 1-phenyl group with the pseudoazulene nucleus is inhibited by the adjacent 9-carbomethoxy and 2-phenyl groupsings. In XLVIII and XLIX it is the phenyl group in position 3 which cannot assume a planar configuration with respect to the five-membered ring due to the proximity of the 2-phenyl and 4-methyl groups. The phenyl groups which are thus prevented from achieving coplanarity with the rest of the molecule will be unable to conjugate with the π electron system of the cyclopentaquinoline nucleus and will not affect the absorption in the visible region of the spectrum.

It is of interest to note that 2-phenyl-4-methyl-9-carbomethoxy-cyclopenta [b] quinoline XLV shows a bathochromic shift of 42 mμ from its decarboxylated analogue XLIV. Position 9 of the cyclopentaquinoline nucleus may be considered equivalent to positions 4 and 8 of azulene and since the carbomethoxy group is electron attracting the observed shift appears in agreement with that expected in azulene. Azulene-4-carboxylates are as yet unknown, but Reid, Stafford and Ward (J., 1958, 1102) predict that the carboxylate group will exert a bathochromic effect as it does

in position 6. From measurements of the visible absorption maxima of the isomeric ethyl 4-methoxyazulenecarboxylates and 4-methoxyazulene, they calculated that a 4- (or 8-) ethoxycarbonyl group may be expected to displace λ max. by +45 mμ . This value is in good agreement with the shift by a methoxycarbonyl (carbomethoxy) group in pseudoazulenes.

Treibs and Kempter (Chem. Ber., 1959, 92, 601) have also investigated the synthesis of pseudoazulenes of the cyclopenta [b] quinoline series and succeeded in preparing 3-phenyl-4,9-dimethylcyclopenta [b]-quinoline L. It is reported as a violet crystalline solid (λ max. in the visible region = 540 mμ in cyclohexane) which dissolves in 80% phosphoric acid with a yellow-greenish colouration.

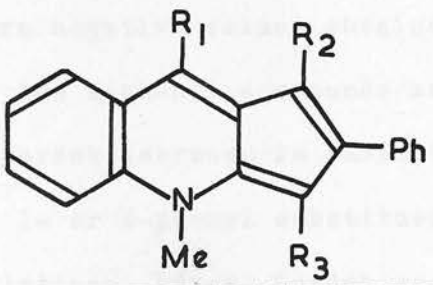
It has been seen (Table III) that 1,2-diphenyl-4-methylcyclopenta [b] quinoline XLVI shows a bathochromic shift of 22 mμ from the 2-phenyl derivative XLIV; this value is in good agreement with the shift of +26 mμ shown by 1-phenylazulene (Table I). In the oxygen series (Table II) phenyl groups in positions 1 and 3 exert almost equal bathochromic shifts, and if the same criterion could be applied to their nitrogen analogues, the still unknown 3-phenyl-4-methylcyclopenta [b] - quinoline would be expected to exhibit a bathochromic shift of ca. 22 mμ from the parent (phenyl unsubstituted) compound. Assuming that the shifts caused by substituents in position 9 of the cyclopenta [b] quinoline nucleus correspond closely to the shifts caused by the same substituents in positions 4 or 8 of azulene, the value of λ max. = 540 mμ (cyclohexane) quoted by Treibs and Kempter for 3-phenyl-4,9-dimethylcyclopenta [b] -

quinoline L can be corrected for the 9-methyl group (-15 mμ in azulene; Plattner and Heilbronner, Helv. Chim. Acta, 1947, 30, 910) to (540 + 15) = 555 mμ ; the parent, 4-methylcyclopenta [b] quinoline would then be expected to absorb at (555 - 22) = 533 mμ . The 2-phenyl derivative absorbs at 532 mμ (ethanol) and even allowing for the difference in solvents, these values, which indicate a hypsochromic of 1 mμ for the 2-phenyl group, are in good agreement with a hypsochromic shift of 2 mμ shown by 2-phenylazulene. No definite conclusions can be drawn until more experimental data are available, but despite the various assumptions used in this calculation, the result appears to point to a close similarity in spectral behaviour on substitution between the cyclopentaquinolines and the azulenes.

The basicities of several pseudoazulenes of the cyclopentaquinoline series were determined and their Ho ($K' = 1$) constants are collected in Table IV; (the plots of $\log_{10} K$ against Ho are shown in Figs. 1 and 2).

TABLE IV.

(Solvent system : Aqueous sulphuric acid-Benzene)

	Ho ($K' = 1$)
XLIV; $R_1 = R_2 = R_3 = H$	+2.80
XLV; $R_1 = COOMe$, $R_2 = R_3 = H$	+1.28
XLVI; $R_1 = R_3 = H$, $R_2 = Ph$	-0.57
XLVII; $R_1 = COOMe$, $R_2 = Ph$, $R_3 = H$	-1.01
XLIX; $R_1 = COOMe$, $R_2 = H$, $R_3 = Ph$	-1.21

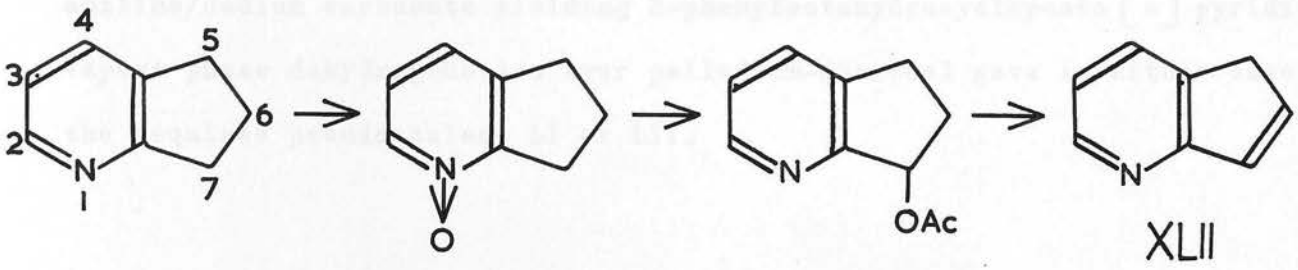
The Ho ($K' = 1$) constants, listed above, can be of value in identification of very small quantities of a pseudoazulene with accuracy, but for previously stated reasons they cannot be taken as strictly quantitative measures of the relative basicities of compounds XLIV-XLIX (Table IV). Two conclusions, however, appear permissible -

(1) The introduction of a carbomethoxy substituent into position 9 of the pseudoazulene nucleus causes a decrease in basicity. This may be attributed to the electron-attracting character of the group, which reduces the polarisation of the system, thus causing a decrease of electronic concentration in the five-membered ring positions exposed to the protonoid attack.

(2) 1,2- and 2,3-Diphenyl derivatives appear less basic than the respective 2-phenyl pseudoazulenes. The more negative values obtained for Ho ($K' = 1$) constants of the diphenyl compounds are in agreement with an apparent decrease in basicity observed on introduction of 1- or 2-phenyl substituents into the azulene nucleus (Plattner, Fürst, Gordon and Zimmermann, Helv. Chim. Acta, 1950, 33, 1910).

In recent years attempts have also been made to synthesise unsubstituted nitrogen analogues of azulene. Prelog and Szpilfogel (Helv. Chim. Acta, 1945, 28, 1684) and later Los and Stafford (J., 1959, 1680) were

unable to prepare the unsubstituted XLII and XLIII through failure to dehydrogenate the corresponding dihydro compounds. In 1958 the successful synthesis of XLII was accomplished by Robison (J.A.C.S., 1958, 80, 6254). The method employed involved the introduction of a functional group in the five-membered ring of 6,7-dihydro-5H-cyclopenta [b] pyridine (1-pyrindane), whose subsequent elimination resulted in unsaturation. This end was attained by rearrangement of 6,7-dihydro-5H-cyclopenta [b]-pyridine-N-oxide on treatment with acetic anhydride.

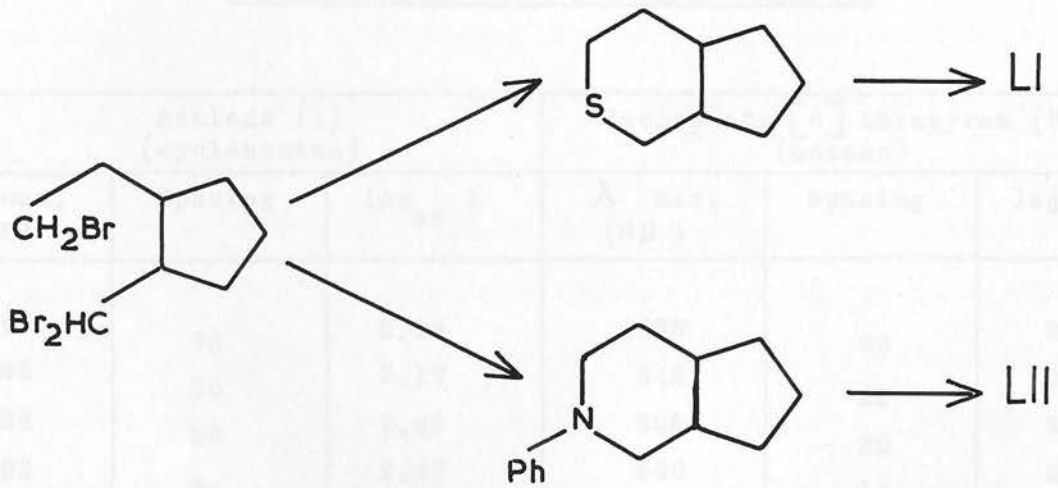


Robison suggested that it is improbable that XLII exists solely as 5H-cyclopenta [b]pyridine or its isomer, 7H-cyclopenta [b] pyridine, but rather that the material is normally a mixture of labile tautomeric forms. Although it appeared to possess a marked stability in strong acid medium, the free base itself was quite unstable and on exposure to the air at room temperature became brown-red in a few hours. A pure sample after repeated distillations was still orange but the orange colour appeared to vanish on dilution with 2-3 volumes of organic solvent and dilute cyclohexane solutions were transparent above 305 mμ .

Anderson, Harrison, Anderson and Osborne (J.A.C.S., 1959, 81, 1255) suggested that Robison's orange impurity in XLII was the parent

nitrogen pseudoazulene, 1H-cyclopenta [b] pyridine, II; X = NH, but no confirmatory experimental evidence has been published. They were successful, however, in the synthesis of two other simple analogues of azulene, cyclopenta [c] thiapyran III; X = S (LI) and 2-phenylcyclopenta [c] pyridine III; X = NPh (LII).

The method employed involved the preparation of β- (2-hydroxymethylcyclopentlyl)-ethanol, which after bromination was treated either with sodium sulphide to give octahydrocyclopenta [c] thiapyran or with aniline/sodium carbonate yielding 2-phenyloctahydrocyclopenta [c] pyridine. Vapour phase dehydrogenation over palladium-charcoal gave in either case the required pseudoazulene LI or LII.



Both compounds were intensely coloured, crystalline solids: the sulphur pseudoazulene was deep red and the nitrogen analogue orange-

yellow. They showed considerable thermal stability and were indifferent to alcoholic alkali but were slowly degraded by dilute sulphuric acid and acetic acid and were decomposed by alumina or silica gel.

The absorption spectra of LI and LII resemble those of azulene but their visible maxima are shifted to shorter wavelengths. The hypsochromic shift is less pronounced in the sulphur pseudoazulene which also resembles the parent hydrocarbon in showing a fine structure of its visible absorption band. The values of λ max. and $\log_{10}\Sigma$ for the individual maxima of the long-wave band of azulene and its sulphur analogue LI are collected in Table V.

TABLE V.

The Fine Structure of the Visible Band of Azulene and Cyclopenta[c]thiapyran.

Azulene (1) (cyclohexane)			Cyclopenta [c] thiapyran (2) (hexane)		
λ max. (mμ)	Spacing	$\log_{10}\Sigma$	λ max. (mμ)	Spacing	$\log_{10}\Sigma$
697	35	2.18	565	23	2.26
662	30	2.18	542	22	2.54
632	29	2.49	520	20	2.54
603	24	2.47	500	17	2.97
579	21	2.52	483	18	3.04
558	17	2.42	465		3.08
541		2.33			

(1) Kloster-Jensen, Kovats, Eschenmoser and Heilbronner, Helv. Chim. Acta, 1956, 39, 1051.

(2) Anderson, Harrison, Anderson and Osborne, J.A.C.S., 1959, 81, 1255.

The visible band of the nitrogen analogue LII entirely lacks any fine structure and there is only a broad single peak at 432 mμ ; this may be attributed to the presence of the 2-phenyl substituent. Like azulene, LI and LII are basic and their visible bands disappear in acid solution.

The aromatic character of cyclopenta [c] thiapyran and its similarity to azulene is also demonstrated by its ability to undergo electrophilic disubstitution (Anderson and Harrison, Tetrahedron Letters, 1960, 11). It is claimed that there is strong evidence that, as in azulene, the electrophilic attack occurs on positions 1 and 3. The synthesis of dichloro-, dibromo-, dithiocyano-, and diacetyl-cyclopenta [c] thiapyrans is reported.

The only other information about electrophilic substitution in pseudoazulenes is given by Treibs and Schroth (Angew. Chem., 1959, 71, 71, 578). They report that benzo [b] indeno [1,2-e] pyran XXXV is readily attacked by electrophilic reagents and that in certain cases they were able to show that substitution occurred at $C_{(6)}$ (which corresponds to positions 1 or 3 in azulene). Although no experimental details are given, Treibs and Schroth claim to have synthesised 6-substituted benzo [b] indeno [1,2-e] pyrans (as XXXV) with, for example, R = NO_2, C_6H_5-N = N-, Halogen, and alkyl. They also claim that XXXV reacts with organo-lithium compounds, resulting in attachment of the nucleophilic organic residue to $C_{(11)}$ (corresponding to positions 4 or 8 in azulene) and that dehydrogenation yields 11-substituted benzo [b]-indeno [1,2-e] pyrans, but again no details are given.

In 1959 Boyd (J., 1959, 55) synthesised highly substituted nitrogen and sulphur pseudoazulenes LIII - LVII which differ from the cyclopenta [b] quinoline compounds XLIV - L and their sulphur and oxygen analogues by their quinonoid structure and by the partial reversal of the orders of stability and of the visible absorption maxima (λmax.) of the analogous nitrogen, sulphur and oxygen pseudoazulenes.

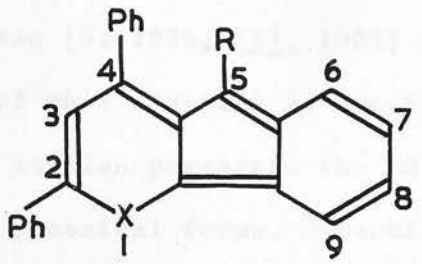


TABLE VI

Compound	λ max.* (mμ)	Colour
LIII; X = NPh, R = H	675	Blue
LIV; X = NPh, R = Ph	685	Bluish-green
LV; X = NMe, R = H	-	Blue
LVI; X = NMe, R = Ph	670	Blue
LVII; X = S, R = Ph	825	Green
LVIII; X = S, R = H LIX; X = O, R = H LX; X = O, R = Ph	not formed	

* Solvent : dioxan.

All compounds in this series possess the unfavourable quinonoid structures and the presence of the phenyl substituents, particularly in the five-membered ring, exerts a stabilising influence over the whole system. Such stabilisation of energetically unfavoured structures by aromatic groups is well known and e.g., tetraphenylcyclopentadienone is stable but cyclopentadienone itself seems incapable of any but the briefest existence (Deschamps, Compt. rend., 1958, 246, 3065). In 1925 Armit and Robinson (J. 1925, 127, 1604) prepared the anhydro-base XXI; the structure of this compound is analogous to the structures LIII - LVII, because it also possesses the unfavourable o-quinonoid ring in its covalent canonical forms. Stabilisation is achieved by fusion to the aromatic cyclopentapyridine system, together with the presence of the phenyl substituent in the five-membered ring, which is important as attempts to isolate the unsubstituted base failed (J. 1922, 121, 827). Similarly, Boyd found that the sulphur pseudoazulene LVII, unlike its nitrogen (N - Ph) analogue, required the presence of a phenyl group in the five-membered ring for its formation (and presumably existence), while even this was not sufficient for the analogous oxygen compound LX. The nitrogen (N-Me) pseudoazulene LV could be formed in the absence of the 5-phenyl substituent but was too unstable for its isolation and purification. Boyd suggested that the varying requirements for the 5-phenyl group, together with the lability of the N-Me compound LV, indicate the following order of decreasing stability in

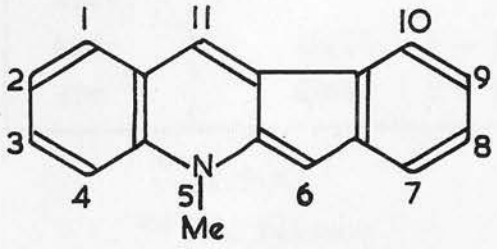
the pseudoazulenes of system II:-

$$X = NPh > NMe > S > O$$

While this order may be applicable to the series of compounds LIII - LX, and possibly to others with a similar quinonoid structure, it is by no means the general rule and in all other noted cases sulphur and oxygen pseudoazulenes were much more stable than their nitrogen analogues.

2-Phenylbenzo [b] cyclopenta [e] thiapyran XXXI, 2-phenylbenzo [b]-cyclopenta [e] pyran XXXIV, and 2-phenyl-4-methylcyclopenta [b] quinoline XLIV constitute a tricyclic series of analogous pseudoazulenes, differing only in the nature of their hetero-atom. Compounds XXXI and XXXIV were stable crystalline solids and their solutions, when kept in darkness, remained unaltered for several months. On the other hand, their nitrogen analogue XLIV could not be obtained in a solid state and its isolation required immediate complexing with 1,3,5-trinitrobenzene, while its solutions rapidly faded from mauve to yellow.

This difference in stability between the sulphur and oxygen pseudoazulenes on the one hand and the nitrogen on the other was even more marked in the tetracyclic series, which was completed by the synthesis of 5-methylindeno [2,1-b] quinoline LXI.



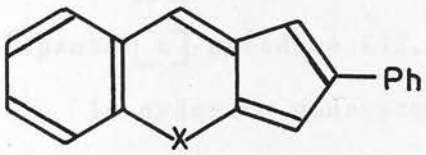
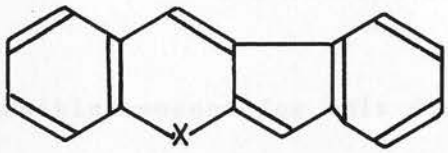
LXI

The sulphur pseudoazulene, benzo[b]indeno[1,2-e]thiapyran XXXII and the analogous pyran XXXV were stable and beautifully crystalline compounds. In contrast LXI was very unstable and was particularly susceptible to atmospheri oxidation and strong sunlight. Thus, in solution, on exposure to sunlight, the decomposition occurred in about one minute, the colour changing from purple-violet to bright green. The indenoquinoline formed a beautifully crystalline 1,3,5-trinitrobenzene derivative which was considerably more stable than the uncomplexed pseudoazulene.

It is of interest to compare the effect of different hetero-atoms on the visible absorption of analogous nitrogen, sulphur and oxygen pseudo-azulenes. Two series of analogous compounds can be considered in detail. The values of their visible absorption maxima (λ max.) are collected in Table VII.

TABLE VII

(Solvent : ethanol)

Tricyclic Series	λ max. (mμ)	Tetracyclic Series	λ max. (mμ)
			
XLIV; X = NMe	532*	LXI; X = NMe	531*
	536**		534
XXXI; X = S	520	XXXII; X = S	500
XXXIV; X = O	470	XXXV; X = O	465

* T.N.B.

** In benzene

Since each series consists of compounds which are formally identical in all respects except in their hetero-atom, the large variations in their absorption maxima can only be attributed to the differences in these atoms. In both series nitrogen pseudoazulenes absorb at the longest wavelength and are followed by the sulphur and oxygen analogues respectively. The order of decreasing wavelengths of the visible absorption maximum is -

$$X = NMe > S > O$$

It has already been indicated that Badger and Christie (J., 1956, 3438) observed a similar order of λmax. (in the near-ultraviolet region) in the more condensed heterocyclic analogues of benzenoid hydrocarbons, e.g., XXVIII - XXX. However, in Boyd's analogous pseudoazulenes, LIV, LVI, and LVII the N > S order is reversed and the sulphur compound LVII absorbs at longer wavelengths than its two nitrogen analogues LIV and LVI (Table VI). Similarly Anderson's cyclopenta [c] thiapyran LI shows a bathochromic shift from 2-phenyl-cyclopenta [c] pyridine LII.

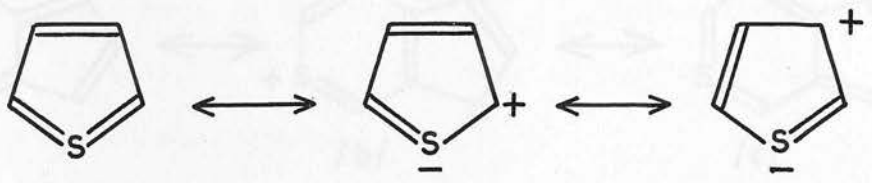
In order to understand the possible reasons for this difference it is necessary to examine the influence which these hetero-atoms exert on the properties of other heterocyclic compounds.

Thus thiophene, furan and pyrrole differ considerably in their properties. Thiophene resembles most closely the parent hydrocarbon and this similarity extends to those properties which are usually believed to depend on mobile electrons and which come under the heading

of "aromatic character". On the other hand, furan and pyrrole, although somewhat aromatic in character, are much less so than thiophene.

One basic difference between sulphur on the one hand and oxygen and nitrogen on the other is that, whereas oxygen and nitrogen have only s and p atomic orbitals available for bonding, sulphur has also five 3 d orbitals in its valence shell. In 1939 Schomaker and Pauling (J.A.C.S., 1939, 61, 1779) suggested that some of these 3 d orbitals may be used for bonding in thiophene.

From consideration of bond lengths, resonance energies, and dipole moments they concluded that in thiophene, in addition to the covalent and dipolar structures, where sulphur obeys the octet rule, the following canonical forms, where it is violated, are also of importance:-



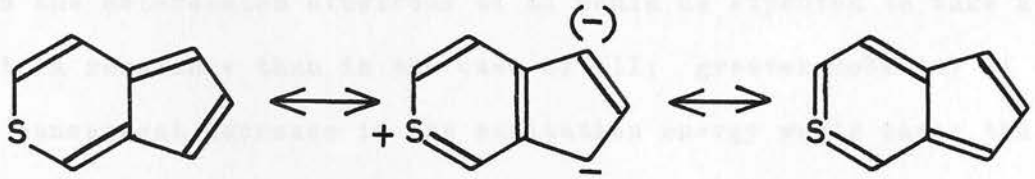
/a/ /b/ /c/

DECET forms.

These forms must involve the sulphur d orbitals for they indicate the expansion of the valence shell of sulphur to accomodate ten electrons; they may thus be referred to as the "decet" forms.

The use of d orbitals in bonding in thiophene involves the hybridisation of one p and two d orbitals ("pd^2 hybridisation" or "d-orbital resonance"); as a result, two sulphur electrons occupy two pd^2 hybrid orbitals and the conjugation with the carbon π electrons is thereby greatly facilitated. Thus the idea of pd^2 hybridisation in thiophene explains its general similarity to benzene and its highly aromatic character (Longuet-Higgins, Trans. Faraday Soc., 1949, 45, 173).

One might therefore expect that in the more complex sulphur heterocyclics also, decet forms would make their contributions to resonance and, for example, cyclopenta [c] thiapyran LI would then be represented as a resonance hybrid of canonical forms, which included the decet structure LI(C).



/a/ /b/ /c/

Octet forms Decet form

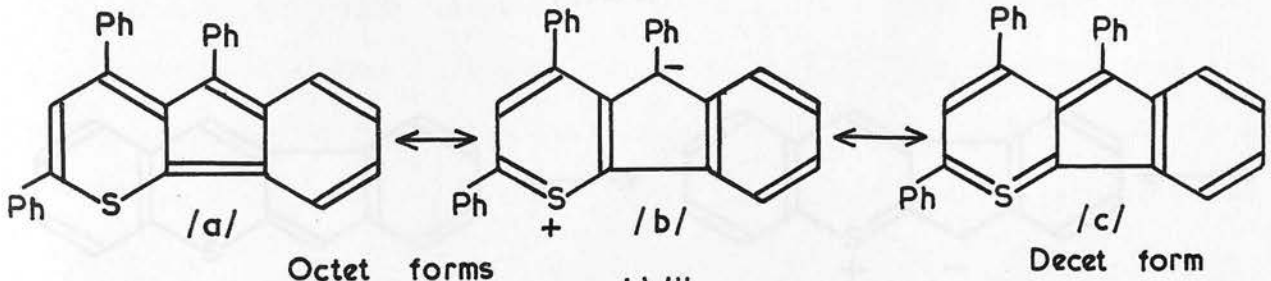
LI

The dipolar decet structures, showing a negative charge associated with sulphur and a positive charge with the five-membered ring, need not be considered here since they would involve the removal of electrons from the neutral five-membered ring, and it is known that for aromatic stability cyclopentadiene must be associated with the negative charge.

It has been seen that in the heterocyclic analogues of azulene dipolar structures of type LI (b) make very significant contributions to the resonance of the system. Recent experimental evidence shows that d-orbital resonance is of greatest importance when positively charged sulphur is located in the vicinity of a carbanion (Henbest, Ann. Reports, 1956). The pseudoazulene system, e.g.,LI, thus offers very favourable conditions for its development, the five-membered ring carbanion being stabilised by resonance between the forms (b) and (c), a decet of electrons developing around sulphur in the latter form.

In view of the above, it is not unexpected that cyclopenta [c]-thiapyran LI absorbs at longer wavelength (visible region) than 2-phenyl-cyclopenta [c] pyridine LII, since while both the octet and the decet forms contribute to the resonance hybrid of the sulphur compound, only the octet forms can contribute to the resonance of its nitrogen analogue. Thus the hetero-atom electrons of LI would be expected to take a greater part in resonance than in the case of LII; greater mobility of electrons and consequent decrease in the excitation energy would cause the absorption to shift to longer wavelengths.

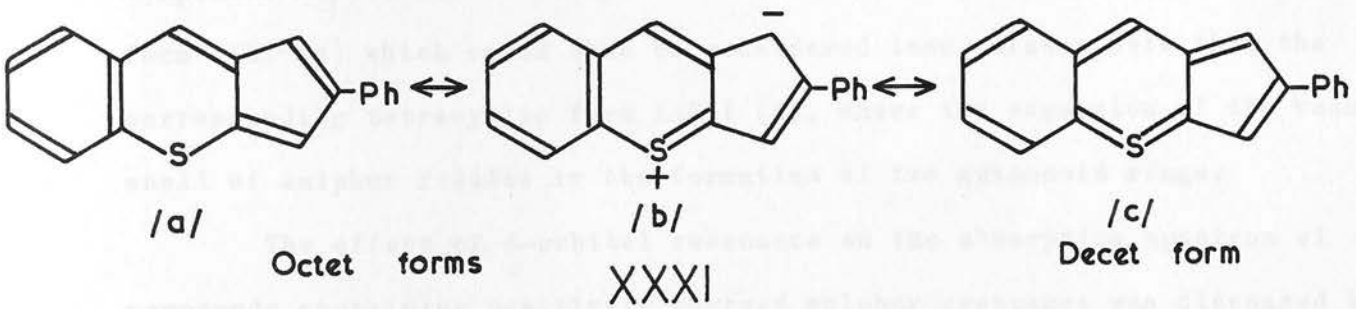
2,4,5-Triphenylindeno [1,2-b] thiapyran LVII appears to represent a particularly favourable system for the development of d-orbital resonance. It can probably be best formulated as a resonance hybrid of the canonical forms -



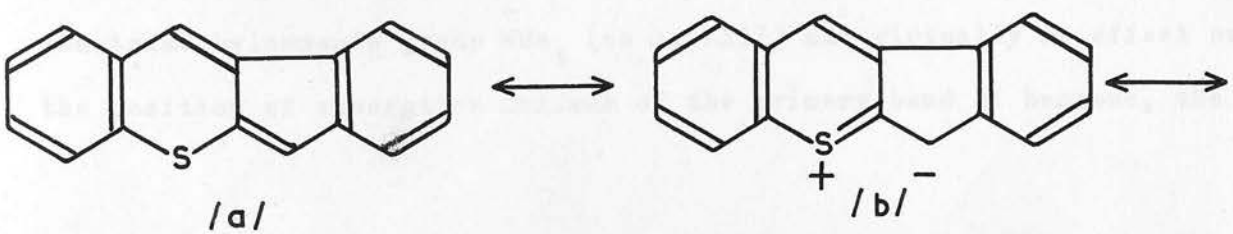
LVII

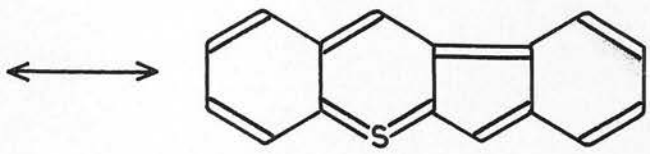
The covalent octet structure LVII (a) is quinonoid and can therefore be expected to be of reduced importance relative to the dipolar structure LVII (b), which shows a positive sulphur in proximity to an anionic carbon centre. The carbanionic system is stabilised by resonance between LVII (b) and the decet form LVII (c) which is of stable Kekulé type and should thus make an important contribution to the hybrid. In agreement with this formulation, LVII shows large bathochromic shifts of 140 mμ and 155 mμ from its nitrogen analogues LIV and LVI, respectively (Table VI).

It has been seen, however, that in the two completed series of analogous pseudoazulenes, the nitrogen compounds XLIV and LXI absorb at longer wavelengths than their sulphur analogues, XXXI and XXXII, respectively (Table VII). This order of the position of the visible absorption maximum could be attributed to the unfavourable conditions for d-orbital resonance in the thiapyrans XXXI and XXXII.



XXXI





/c/

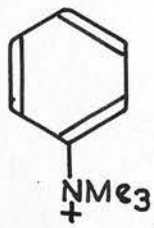
Decet form

XXXII

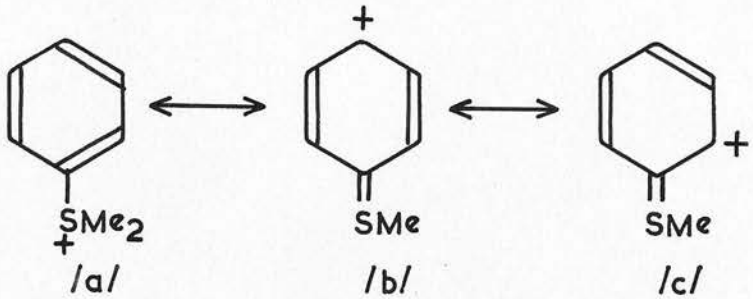
This time it is the covalent octet structures XXXI (a) and XXXII (a) that are of Kekulé form and must therefore contribute substantially to resonance, while the decet structures XXXI (c) and XXXII (c) are of the unfavourable quinonoid type and their contribution to the hybrid can be expected to be very much less significant than the contribution of the corresponding structure in LVII.

The bathochromic shifts shown by nitrogen compounds XLIV and LXI from the sulphur analogues XXXI and XXXII respectively differ in the two series of pseudoazulenes (Table VII). The smaller difference in the tricyclic compounds may be due to the presence of only one quinonoid ring in the decet form XXXI (c) which could thus be considered less unfavourable than the corresponding tetracyclic form XXXII (c), where the expansion of the valence shell of sulphur results in the formation of two quinonoid rings.

The effect of d-orbital resonance on the absorption spectrum of compounds containing positively charged sulphur groupings was discussed by Bordwell and Boutan (J.A.C.S., 1956, 78, 87). They observed that while the trimethylammonio group $\overset{+}{N}Me_3$ (as in LXII) had virtually no effect on the position of absorption maximum of the primary band of benzene, the

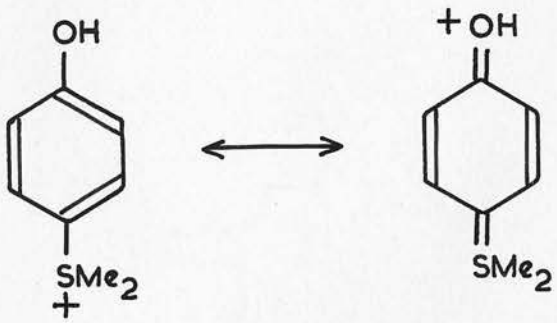


LXII



LXIII

dimethylsulphonio group $\overset{+}{S}Me_2$ (as in LXIII) caused a bathochromic shift of 17 mμ. This was attributed to the stabilisation of the cation LXIII by resonance between the forms LXIII (a), (b) and (c), a decet of electrons developing around sulphur in the latter forms. In addition, they noted that the trimethylammonio group did not greatly affect the absorption maximum when substituted into a position para to an electron releasing group, such as a hydroxyl. On the other hand, the primary band of benzene, which was shifted from 203 mμ to 220 mμ by substituting a dimethylsulphonio group, was further shifted to 242 mμ in p-$Me_2\overset{+}{S}$-C_6H_4-OH (p-dimethylsulphonio-phenol). They accounted for it by assuming a conjugative interaction between $\overset{+}{S}Me_2$ and OH groupings, which is represented in resonance terminology by forms such as LXIV (a) and (b).



LXIV

Bordwell and Boutan (J.A.C.S., 1956, 78, 854) also investigated the possibility of d-orbital resonance (electron-pair acceptor type conjugation for sulphur) with uncharged sulphur compounds. They found that the large bathochromic shift caused by conjugative interaction of the RS with C_6H_5 was generally enhanced by the introduction of a p-nitro and similar groups but remained almost unchanged by the introduction of a p-hydroxy group and they therefore suggested that it seemed to be best interpreted as an electron-pair donor type conjugative effect for sulphur.

Quantitative assessment of resonance interactions can usually also be obtained from comparative measurements of ionisation constants of meta- and para-substituted acids, amines, etc. In the para-substituted series (e.g., MeS as potential electron acceptor), Bordwell and Boutan could not discern any d-orbital resonance even when a p-oxyanion was present as the potential electron donor. They concluded that both acidity constants and ultraviolet spectral measurements indicate that d-orbital resonance with uncharged sulphur compounds is probably of importance only with carbanions.

The use made by Bordwell and Boutan of spectral measurements to evaluate resonance interactions in sulphur compounds is based on evidence of Doub and Vandenbelt (J.A.C.S., 1947, 69, 2714; 1949, 71, 2414) who clearly demonstrated that conjugative effects existing in the ground state of p-substituted benzenoid derivatives are very frequently

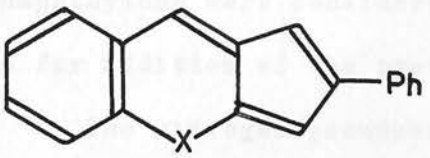
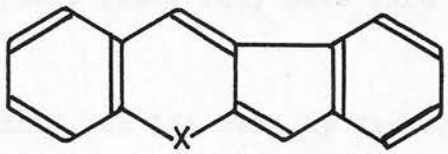
reflected in the excited states responsible for their ultraviolet absorption spectra by shifts of absorption maxima to longer wavelengths.

It is of interest to note at this stage that while the principal absorption band of p-nitroaniline is at 374 mμ , the absorption of p-nitrobenzenethiol is shifted to 315 mμ . In view of the findings of Bordwell and Boutan, d-orbital resonance in the latter must be unimportant and is made even more so by the presence of the electron-attracting p-nitro group. The bathochromic shift shown by p-nitroaniline from its sulphur analogue thus appears in agreement with similar shifts (visible spectrum) shown by nitrogen pseudoazulenes XLIV and LXI from the sulphur analogues XXXI and XXXII respectively, which could also be attributed to the unimportance of d-orbital resonance in the sulphur compounds. Similarly conclusions of Bordwell and Boutan that the bathochromic shifts shown by dimethylsulphoniophenyl compounds from their trimethylammoniophenyl analogues must be attributed to d-orbital resonance in the former, appear in agreement with observations in pseudoazulenes, for when conditions for d-orbital resonance are favourable, sulphur compounds LI and LVII absorb at longer wavelengths than the nitrogen analogues LII and LIV or LVI respectively.

The basicities of the two complete series of analogous nitrogen, sulphur and oxygen pseudoazulenes were determined and the plots of $\log_{10} K'$ against Ho are shown in Figs. 1,2, and 3; Ho ($K' = 1$) constants are collected in Table VIII.

TABLE VIII.

(Solvent system : Aqueous sulphuric acid - Benzene)

Tricyclic Series			Tetracyclic Series		
		Ho(K'=1)			Ho(K'=1)
XLIV	X = NMe	+2.80	LXI;	X = NMe	+2.77
XXXIV;	X = O	-2.00	XXXV;	X = O	-4.20
XXXI;	X = S	-2.66	XXXII;	X = S	-4.25

A strict quantitative comparison of the basicities of analogous pseudoazulenes is not possible, since it would involve the assumption that the true distribution coefficient of the free pseudoazulene between the inert solvent and the aqueous layer was the same for the compounds to be compared (cf. Heilbronner, "Azulenes" in "Non-Benzenoid Aromatic Compounds"), but certain observations and comparisons of a general character may be permissible, as is indicated by the study of recent literature. Thus Plattner, Fürst and Keller (Helv. Chim. Acta, 1949, 32, 2464) examined the Ho (K' = 1) constants of the benzazulenes and the alkyl azulenes and concluded that the fusion of a benzene ring lowers the basicity of azulene, in contrast to the alkyl substitution which increases it; comparison was also made of the Ho (K' = 1) constants of 1,2- and 5,6-benzazulenes and deductions were drawn from the fact that the latter appears less basic. The basicities of azulene and 5,6-benzazulene were

contrasted by Reid, Stafford and Ward (J. 1955, 1193) who considered that a general comparison was possible since in both compounds there are two positions which can act as proton acceptors. Similarly 1,2-benzazulene and the newly synthesised azulenic cyclohepta [bc]-acenaphthylene were considered comparable since they have each one site for addition of the proton.

The nitrogen pseudoazulenes XLIV and LXI were by far the most basic and appeared to possess very similar basicities in both series (Table VIII). The lesser basicities of the oxygen compounds XXXIV and XXXV are in agreement with the more electronegative character of the oxygen atom. If the electronegativity of the hetero-atom is high it is unwilling to part with its electron pair, (its 2 p orbital is "contracted" relatively to the carbon 2p (π) orbitals), so that little conjugation can occur. Thus in the oxygen pseudoazulenes hetero-atom electrons are less readily available then in the analogous nitrogen compounds and consequently contributions of the betaine forms (as XX (b) and (c)) will be less important, resulting in decreased polarisation and lesser basicity.

The nitrogen pseudoazulenes XLIV and LXI are also clearly very much more basic than the sulphur analogues XXXI and XXXII and this despite the greater electronegativity of the nitrogen atom. This order of basicity can probably be explained by the fact that while nitrogen, like carbon (and oxygen), is in the first short period of the Periodic Table, sulphur is the second. Thus although the screening

action of inner electron shells makes sulphur less electronegative than nitrogen, the tautomeric (+T) effect, which depends on the degree of overlap between 3 p orbital of sulphur and 2 p orbital of carbon, must be greatly diminished by their unequal distance from the bond axis. This results in lower polarisation in sulphur compounds and in N>S order of basicity.

Oxygen is more electronegative than both sulphur and nitrogen but shares with the latter the advantage over sulphur in being located in the first short period of the Periodic Table along with carbon. The available results (Table VIII) would seem to indicate that the basicities of the analogous oxygen and sulphur compounds are not too different, but no definite conclusions can be drawn, firstly because, as has already been stated, the Ho ($K' = 1$) constants cannot be taken as quantitative measures of the relative basicities and secondly, because of the lack of a good agreement in the two series of compounds listed in Table VIII.

In the tricyclic series, following the very basic nitrogen compound XLIV, the oxygen pseudoazulene XXXIV appears somewhat more basic than the sulphur analogue XXXI. It is of interest to note that Bordwell and Boutan (J.A.C.S., 1956, 78, 854) obtained rather similar results from measurements of the acidity constants of m- and p-substituted benzoic acids and phenols, for they concluded that the order of conjugation in such compounds was -

$$Me_2N > MeO > MeS \quad \text{and}$$

$$MeCONH > MeCOO > MeCOS$$

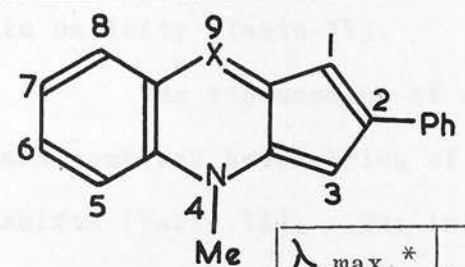
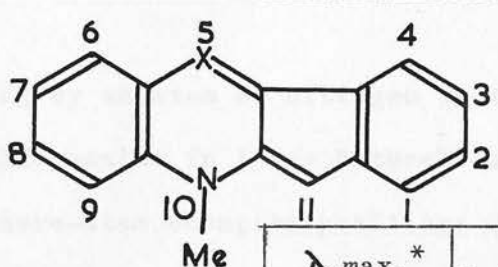
This order also appears to be borne out by the results of aromatic substitution (Bordwell and Boutan, loc cit; Van Horne, Bull. sci. acad. roy. Belg., 5 , 1927, 13, 206; Suter, Mackenzie and Maxwell, J.A.C.S., 1936, 58, 717).

The two series of analogous nitrogen, sulphur and oxygen pseudoazulenes (Tables VII and VIII) were extended by the synthesis of 2-phenyl-4-methylcyclopenta [b] quinoxaline LXV and 10-methylindeno-[2,1-b] quinoxaline LXVI. They are the heterocyclic analogues of the still unknown 2-phenyl-4-aza-5,6-benzazulene and 4-aza-2,3,5,6-dibenzazulene, respectively. The values for the wavelengths of their visible absorption maxima (λ max.) and the Ho (K' = 1) basicity constants are listed in Table IX.

TABLE IX.

Absorption Spectra; Solvent : Ethanol

Ho (K' = 1) constants; Solvent system : Aqueous sulphuric acid-Benzene.

					
	λ max.* (mμ)	Ho(K'=1)		λ max.* (mμ)	Ho(K'=1)
XLIV; X = CH	532	+2.80	LXI; X = CH	531	+2.77
LXV; X = N	599	+1.07	LXVI; X = N	579	+0.28

vid. Table XII

Compound LXV (the pseudoaza-azulene) was a beautifully crystalline dark blue solid and was more stable than the analogous pseudoazulene XLIV, which could only be obtained in the solid state in the form of its 1,3,5-trinitrobenzene derivative. The tetracyclic pseudoaza-azulene LXVI was deep violet and crystalline, but unlike the analogous pseudoazulene LXI and the tricyclic compound LXV, it did not react with 1,3,5-trinitrobenzene and could only form a molecular complex with 2,4,7-trinitrofluorenone.

Compounds LXV and LXVI are less basic than the analogous pseudoazulenes XLIV and LXI, respectively. This decrease in basicity may be attributed to the electron-attracting character of the second nitrogen atom which reduces the degree of charge separation in the system, thus causing an attenuation of the charge density in position(s) exposed to the protonoid attack. In its action, the second atom of nitrogen resembles the carbomethoxy group, which when introduced into position 9 of the cyclopentaquinoline nucleus also causes a decrease in basicity (Table IV).

The replacement of a CH grouping by an atom of nitrogen in the six-membered hetero-ring of XLIV and LXI results in large bathochromic shifts (Table IX). The introduced hetero-atom occupies positions 9 and 5 in the cyclopentaquinoxaline (LXV) and the indenoquinoxaline (LXVI) nuclei, respectively, and since these positions may be considered equivalent to positions 4 and 8 of azulene and to position 9 in the

cyclopentaquinoline nucleus (XLIV), the ring nitrogen in the two pseudoaza-azulenes appears to act in much the same way as an electron attracting substituent in the above systems. The same effect is observed in sulphur compounds, the pseudoaza-azulene benzo [b] indeno [1,2-e] -[1,4]-thiazine XXXIII (nitrogen atom in position 5) showing a bathochromic shift from the analogous thiapyran XXXII.

The analogy between an annular nitrogen and an electron-attracting substitutent is not confined to pseudoazulenes but can be apparently extended to the azulenes. The values for the wavelengths of the visible absorption maxima of the three aza-azulenes and their parent hydrocarbons and of the three known pseudoaza-azulenes and their pseudo-azulene analogues are collected in Table X.

TABLE X.

COMPOUND	(a) Solvent	(b) $\lambda_{max.}$ (mμ)	$\Delta\lambda_{max.}$ (mμ)	Ref.
2-Phenyl-4-methylcyclopenta[b]quinoline XLIV	Et.	532		*
2-Phenyl-4-methylcyclopenta[b]quinoxaline LXV	Et.	599	+67	*
5-Methylindeno[2,1-b]quinoline LXI	Et.	531		*
10-Methylindeno[2,1-b]quinoxaline LXVI	Et.	579	+48	*
Benzo[b]indeno[1,2-e]thiapyran XXXII	Et.	500		*
Benzo[b]indeno[1,2-e]-[1,4]-thiazine XXXIII	Et.	519	+19	*
Azulene	Et.	577 (c)		1
1-Aza-azulene	Me	460	-117	2
1,3-Diaza-azulene	Me	390 (d)	-187	3
1,2-Benzazulene	Et.	611 (c)		1
1-Aza-2,3-benzazulene	Et.	500	-111	4

* Vid. Table XII

(a) Et = ethanol; Me = methanol.

(b) Unless otherwise stated, the highest point of the broad band was assumed to coincide with the principal (most intense) maximum.

(c) The principal maximum.

(d) Absorption spectrum of the hydrate.

References

(1) Kloster-Jensen, Kovats, Eschenmoser, and Heilbronner, Helv. Chim. Acta, 1956, 39, 1051.

(2) Nozoe, Seto, Matsumura, and Terasawa, Chem. and Ind., 1954, 1357.

(3) Nozoe, Mukai, and Murata, J.A.C.S., 1954, 76, 3352.

(4) Anderson and Tazuma, J.A.C.S., 1952, 74, 3455.

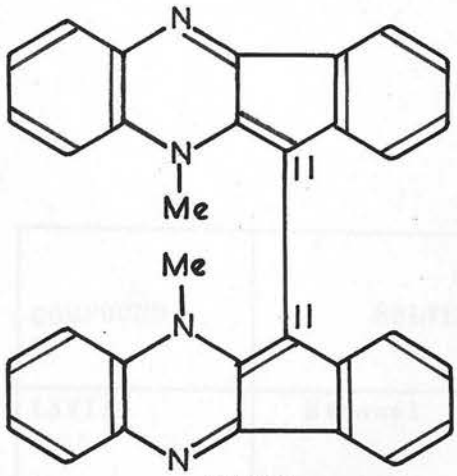
It will be seen that the aza-azulenes all show very large hypsochromic shifts from the carbocyclic compounds. The direction of the shifts is in agreement with the expectations for azulenes carrying electron-attracting substituents in equivalent positions; the extent of the shifts, however, indicates that an atom of nitrogen in the five-membered ring has a much more profound effect on the azulene system than a substituent. The shifts shown by the pseudoaza-azulenes have already been discussed and appear to follow a similar pattern to those observed in the aza-azulenes listed in Table X, but they are very much

smaller and correspond more closely in size to the shifts caused by substituents in azulenes.

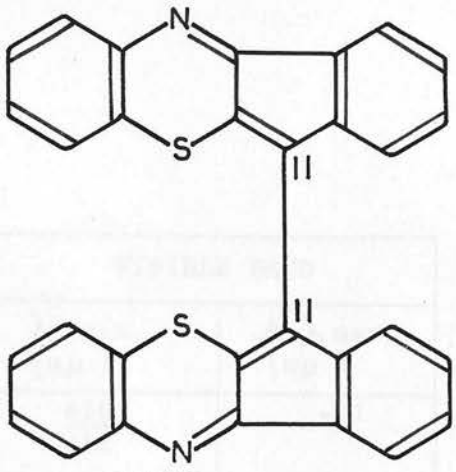
Unfortunately the simple aza-azulenes with the hetero-atom in the seven-membered ring are still unknown. Treibs and Schroth (Angew. Chem., 1959, 71, 71) reported the synthesis of 3-cyano-4-aza-1,2,6,7-dibenzazulene but since the carbocyclic analogue is unknown, the effect of replacing a CH group by N in the seven-membered ring of azulene cannot be at present evaluated.

The two nitrogen pseudoaza-azulenes LXV and LXVI differ in their stability, for although the tetracyclic compound LXVI remains unaltered for long periods in the solid state, on refluxing in presence of air it gradually dimerises to a stable blue solid. The tricyclic compound LXV does not undergo a similar dimerisation.

The dimeric structure for the blue compound is suggested by analysis, molecular weight (by mass spectrometry), and the mode of its formation. In agreement with the structure of pseudoazulenes as formulated in XX, the monomeric compound LXVI must have its greatest electronic concentration in the 11-position. It is therefore concluded that the oxidative dimerisation will occur by linkage at the two free five-membered ring positions as indicated in structure LXVII. The dimer of the sulphur pseudoaza-azulene XXXIII was also isolated and for similar reasons may be assigned structure LXVIII.



LXVII



LXVIII

Both compounds, LXVII (blue) and LXVIII (violet) were stable, high-melting solids and were found to be considerably less basic than their respective monomers (Fig. 4). Since the basicity of the monomeric systems LXVI and XXXIII is associated with their 11-positions, the lower basicity of the dimers appears to confirm the mode of linkage indicated in the structural formulae.

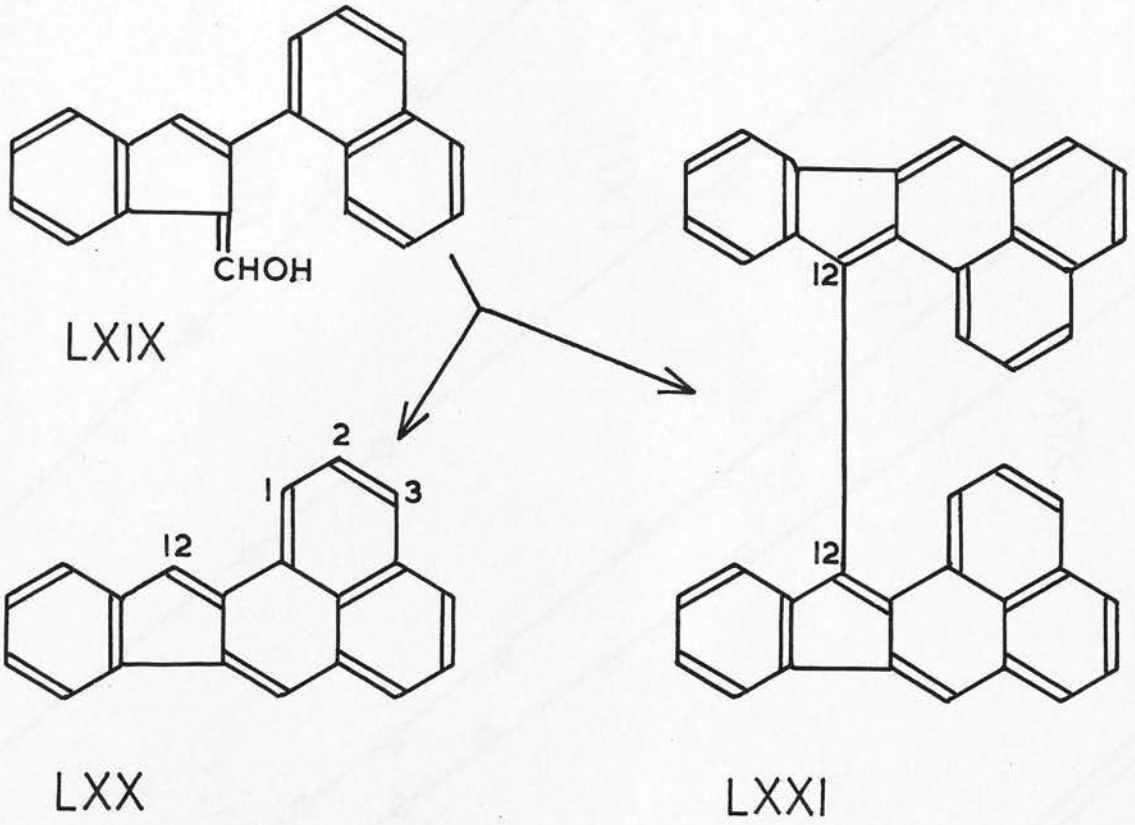
The absorption spectra of the two dimers resembled those of their respective monomers; this similarity is consistent with structures LXVII and LXVIII. In either case, however, the visible absorption band of the dimer was split into two flat peaks, the more intense maximum showing a bathochromic shift ($\Delta \lambda$ max.) from the single broad band maximum of the monomer. The values for λ max. (visible region) of the two dimers and for the shifts $\Delta \lambda$ max. from their respective monomers are collected in Table XI.

TABLE XI

COMPOUND	SOLVENT	VISIBLE BAND	
		λ max. (mμ)	$\Delta\lambda$ max. (mμ)
LXVII	Ethanol	610 411	+31
LXVIII	Tetrahydrofuran	572 514	(+53)[a]

(a) Absorption spectrum of monomer XXIII was taken in ethanol.

The confirmatory evidence for the structures LXVII and LXVIII comes from the work of Aitken and Reid (J., 1956, 3487). They obtained a purple-black hydrocarbon as a bye product in the acid cyclisation of 1-(1-hydroxymethylene-2-indenyl)naphthalene LXIX to indeno[2,1-a] perinaphthene LXX and suggested for its structure LXXI, which is analogous to structures LXVII and LXVIII in that it represents a union of two indenoperinaphthene nuclei at the 12- (five-membered ring) positions, with which the basicity of the monomeric compound can also be associated.



Compound LXX represents a new class of basic hydrocarbons; the accession of the proton is considered to occur to $C_{(12)}$, resulting in the formation, in the perinaphthene moiety, of the twelve π-electronic system of the perinaphthenylium cation. The authors suggest that the low basicity of the purple-black compound indicates that the indenoperinaphthene nuclei are attached at the 12-positions. The molecular weight and analytical data are quoted as supporting structure LXXI. The visible absorption spectra of the dimer (crimson solution in benzene) and the monomer (red solution) are very similar, but as in LXVII and LXVIII, the broad band of the former appears to be segmented into two principal flat maxima, while the latter (in an apolar hydrocarbon solution) shows a more clearly developed fine structure.

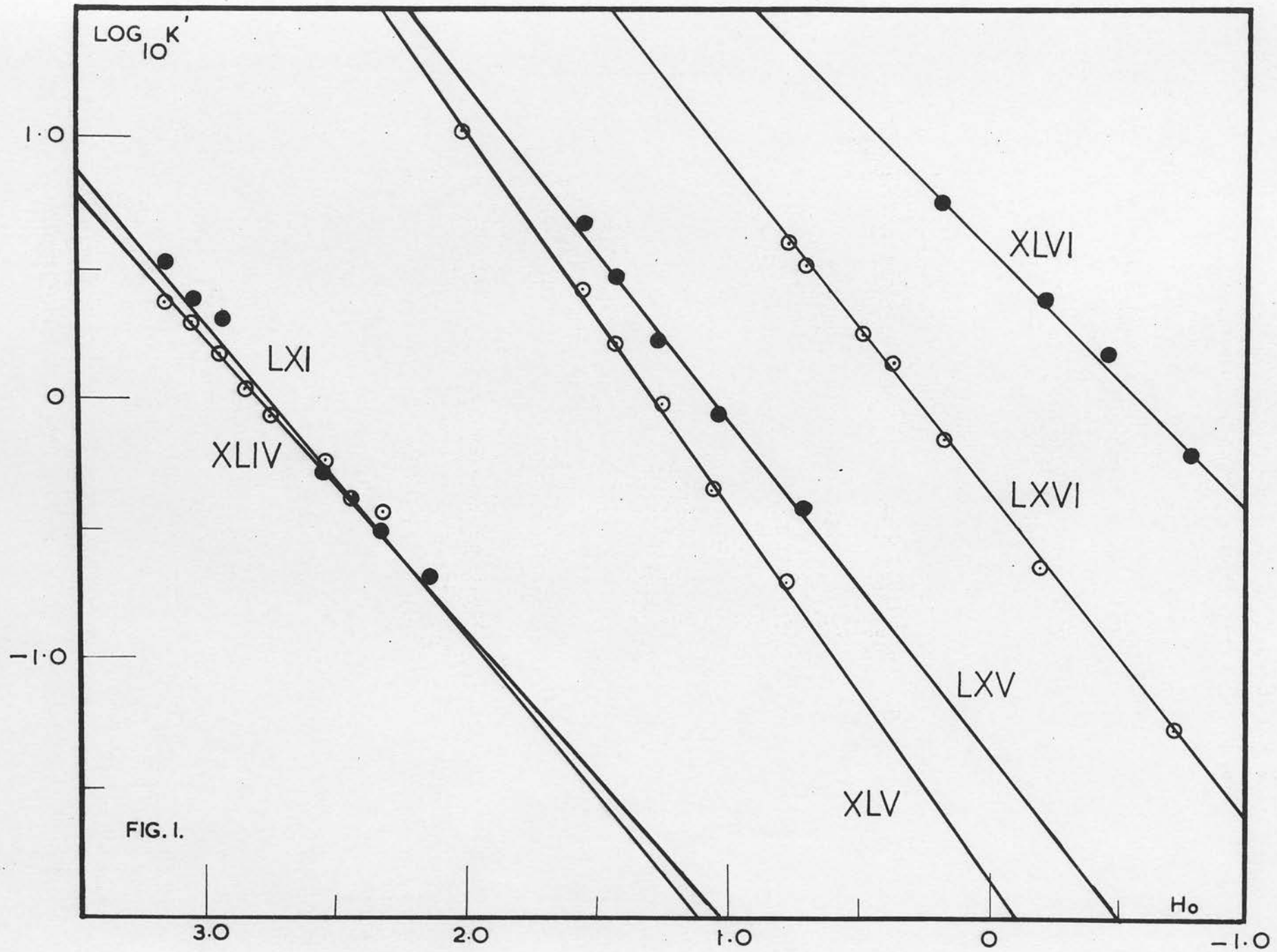


FIG. 1.

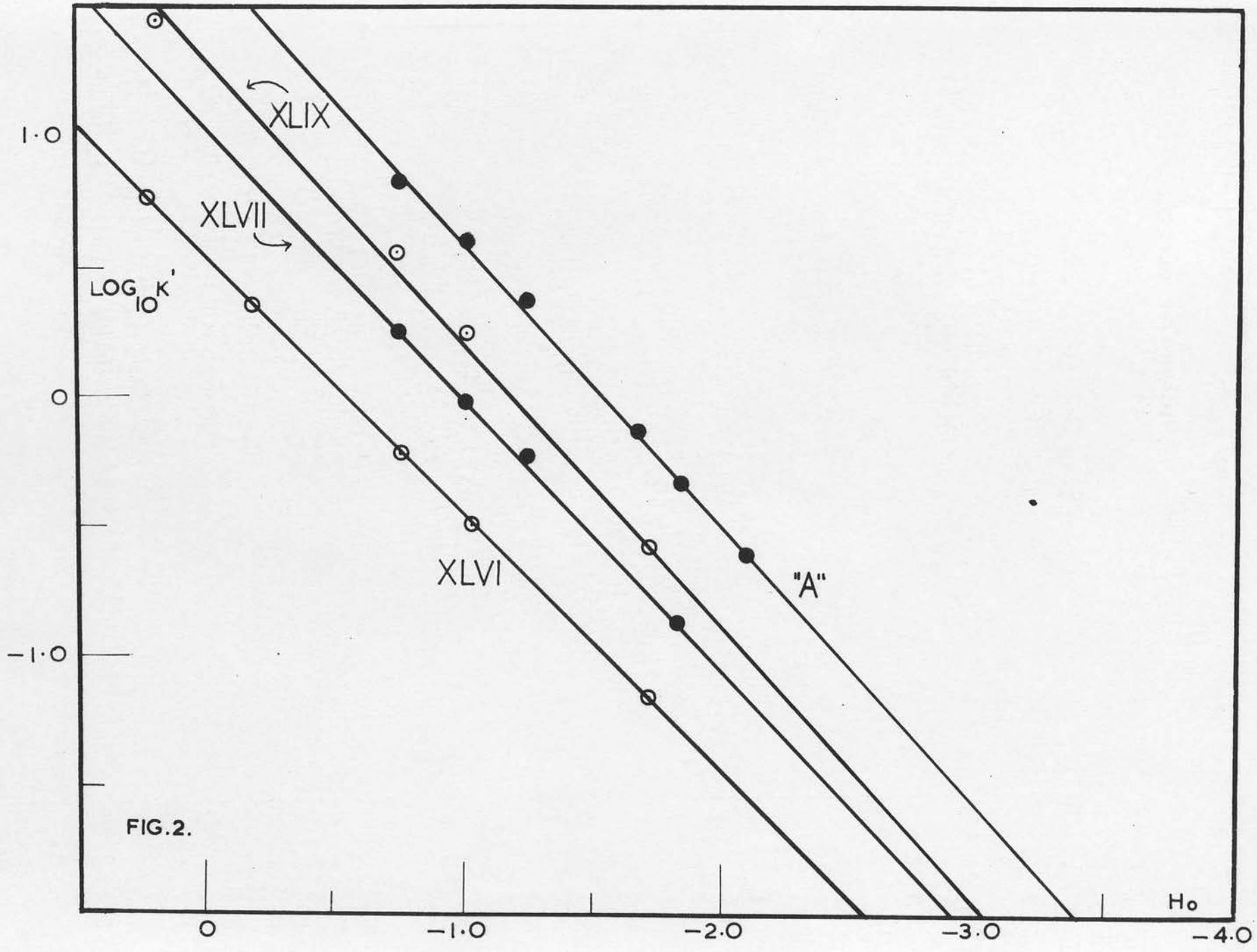


FIG.2.

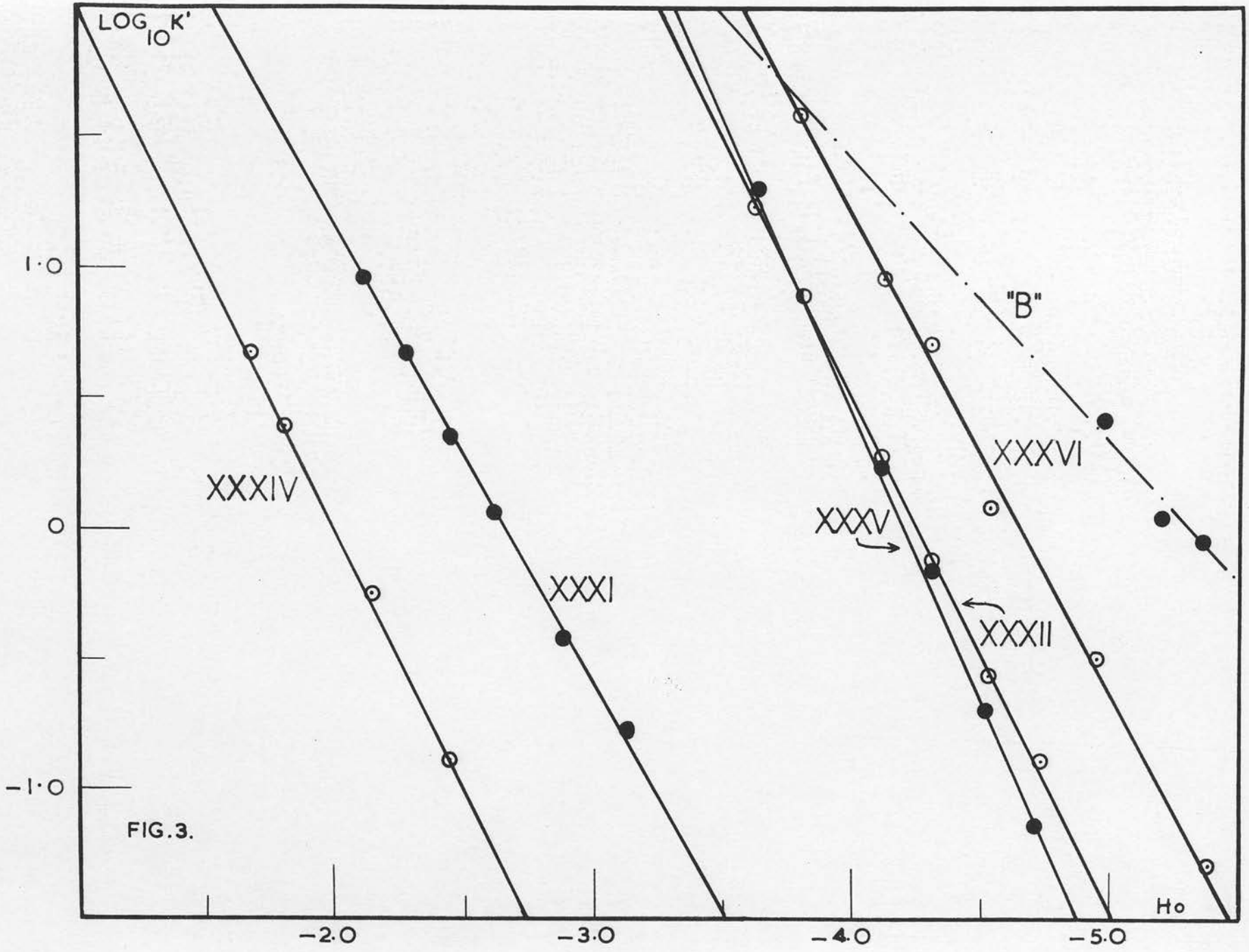


FIG. 3.

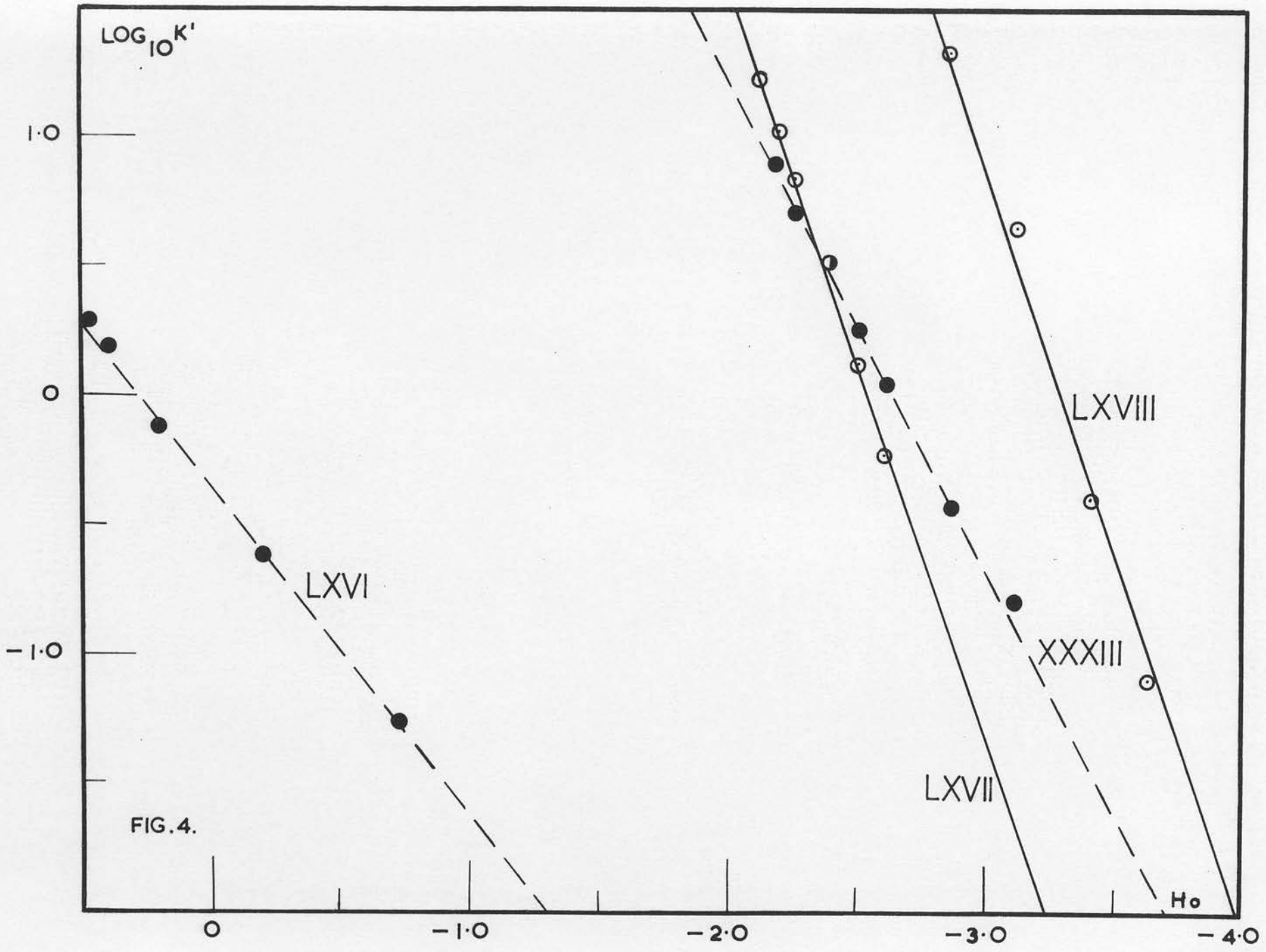
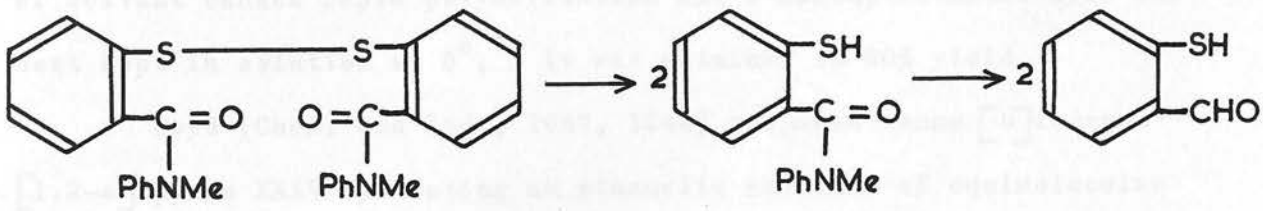


FIG. 4.

DISCUSSION OF EXPERIMENTAL

The preparation of o-mercaptobenzaldehyde represented the initial stage in the synthesis of the sulphur pseudoazulenes XXI and XXXII. Although it was first prepared in 1912 (Friedländer and Lenk, Ber., 1912, 45, 2083) it is a very little studied compound and there is only one recent reference by Weygand, Eberhardt, Linden, Schäfer, and Eigen (Angew. Chem., 1953, 65, 525). Friedländer and Lenk converted o-aminobenzaldehyde by diazotisation and treatment with copper thiocyanate to o-thiocyanatobenzaldehyde, which on warming with sodium sulphide, followed by acidification, yielded the required product. It is reported as an unstable, rapidly resinifying, yellow oil and was not subjected to a direct analysis; no yield was given.

The procedure adopted by Weygand et al. appeared more satisfactory. These authors prepared the aldehyde by a controlled reduction of the N-methylanilide of o-mercaptobenzoic acid with lithium aluminium hydride and isolated it as the 2,4-dinitrophenyl-hydrazone, but the full experimental details were not given. The reaction appears to be a general one and the authors found it applicable to N-methylanilides of a number of aromatic and aliphatic acids.

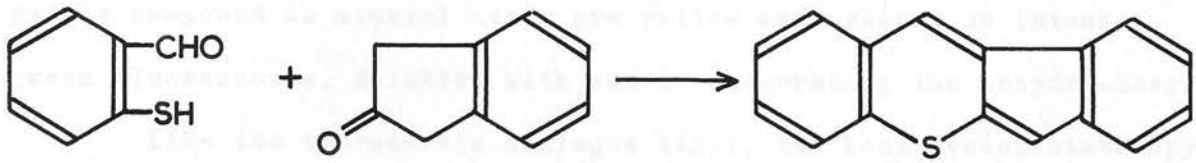


The readily available diphenyl disulphide 2,2'-dicarboxylic acid ("dithiosalicylic acid") was used as a starting material. It yielded a crystalline acid chloride (Reissert and Manns, Ber., 1928, 61, 1312) which with N-methylaniline, in the presence of pyridine, afforded the corresponding N-methylanilide in an almost quantitative yield. The latter was also obtained in a similar yield by treatment of the ester of dithiosalicylic acid with the iodo-magnesium compound of the anilide (cf. Bodroux, Compt. rend., 1904, 138, 1427; Kuhn and Morris, Ber., 1937, 70, 856). Reduction of the disulphide linkage with zinc dust in acetic acid yielded the crystalline N-(o-mercapto-benzoyl)-N-methylaniline in 82% yield.

The lithium aluminium hydride reduction of the anilide to the aldehyde was found to give best results when carried out below 0^{o} (allowing 0.5 mole of hydride/methylanilide group with an additional 0.25 mole for the mercapto group, which, however, does not interfere with the reaction). Friedländer and Lenk (loc. cit.) recommended purification of the aldehyde by steam distillation, but such treatment was found to accelerate its resinification. The aldehyde was therefore isolated by direct extraction of the acidified solution. The removal of solvent causes rapid polymerisation and o-mercaptobenzaldehyde was best kept in solution at 0^{o}. It was obtained in 60% yield.

Boyd (Chem. and Ind., 1957, 1244) prepared benzo [b] indeno-[1,2-e] pyran XXXV by heating an ethanolic solution of equimolecular

amounts of salicylaldehyde and indan-2-one in the presence of piperidine acetate. When salicylaldehyde was replaced by o-mercaptobenzaldehyde, the corresponding dark red thiapyran XXXII was obtained in good yield.



XXXII

The formulation of the red compound as XXXII follows from its analysis, from the similarity of its absorption spectrum to that of the analogous pyran XXXV, and from the method of its preparation. Like XXXV, it dissolved in mineral acids giving deep yellow solutions which exhibited an intense greenish-yellow fluorescence.

Attempts to prepare 2-phenylbenzo [b] cyclopenta [e] thiapyran XXXI by condensation of 3-phenylcyclopent-2-en-1-one (Winternitz et al., Bull. Soc. chim., 1953, 196) and o-mercaptobenzaldehyde, under the conditions employed for the synthesis of XXXII, resulted in a mixture of products. Chromatography on alumina resulted in isolation of two intensely coloured compounds, the reddish-purple, crystalline thiapyran and a deep blue unstable oil.

The formulation of the reddish-purple compound as XXXI follows from its analysis, from its stability and crystalline character in which it resembles XXXII, and from the similarity of its absorption spectrum to those of the analogous oxygen and nitrogen pseudoazulenes, XXXIV and XLIV respectively (Fig. **5**). Solutions of the reddish-purple compound in mineral acids are yellow and exhibit an intense green fluorescence, dilution with water regenerating the anhydro-base.

Like the tetracyclic analogue XXXII, the benzocyclopentathiapyran XXXI can be placed alongside the oxygen pseudoazulenes and the azulenes in order of basicity. The slopes of the straight line plots of log K' against Ho of the sulphur pseudoazulenes XXXI and XXXII are also almost identical with those of the oxygen analogues XXXIV and XXXV respectively and approximate very closely to two (Fig. 3). This has also been found for the azulenes (Plattner, Heilbronner and Weber, Helv. Chim. Acta, 1949, 32, 574) and for indeno [2,1-a] perinaphthene (Aitken and Reid, J., 1956, 3487). Gold and Tye (J., 1952, 2181) examined the basicities of three substituted ethylenes (1,1-dephenyl-ethylene, 1-α-naphthyl-1-phenylethylene, and triphenylethylene) by similar partition experiments and although the acidities involved were considerably higher, the plots of log K' against Ho were also linear with slopes approximately equal to two. They interpreted this result as arising from a salting-in effect on the hydrocarbon base molecules with increasing acidity.

It has now been found that the slopes of all the monomeric nitrogen pseudoazulenes are approximately equal to one (Figs. 1 and 2), while those of the oxidative dimers (both the nitrogen LXVII and the sulphur LXVIII analogues) are almost identical and approximate very closely to three (Fig. 4). The slopes of the "basicity" plots may thus be of value in identification of pseudoazulenes.

The blue compound, formed alongside XXXI in the condensation of o-mercaptobenzaldehyde and 3-phenylcyclopent-2-en-1-one, could not be obtained in an absolutely pure state and its chromatographic eluates were always contaminated with the thiapyran. Its formation in the atmosphere of nitrogen excludes the possibility that it is an oxidation product of XXXI.

The blue compound was very unstable: it was degraded by alumina and its solutions rapidly turned pale yellow. Unlike the sulphur and oxygen pseudoazulenes, it formed a complex with 2,4,7-trinitrofluorenone, which was, however, almost as unstable as the oily substance itself and could not be obtained pure. The blue material was basic and dissolved in mineral acids with a yellow colour but without any fluorescence. The slope of its straight line plot of log K' against Ho (Fig. 2; "A") is approximately equal to one, while those of the sulphur and oxygen pseudoazulenes approximate closely to two. The absorption spectrum of the trinitrofluorenone complex is completely different from the spectrum of XXXI and other pseudoazulenes. No satisfactory structure could be

suggested for the compound.

The yield of the thiapyran XXXI obtained from the direct condensation of o-mercaptobenzaldehyde and 3-phenylcyclopent-2-enone was very small and attempts were therefore made to prepare it by a two stage process involving the initial formation of the benzothiapyrylium salt.

The formation of the benzopyrylium salts has been extensively investigated by Decker and von Fallenberg, Perkin and Robinson, Bülow, Le Fèvre, and by others.

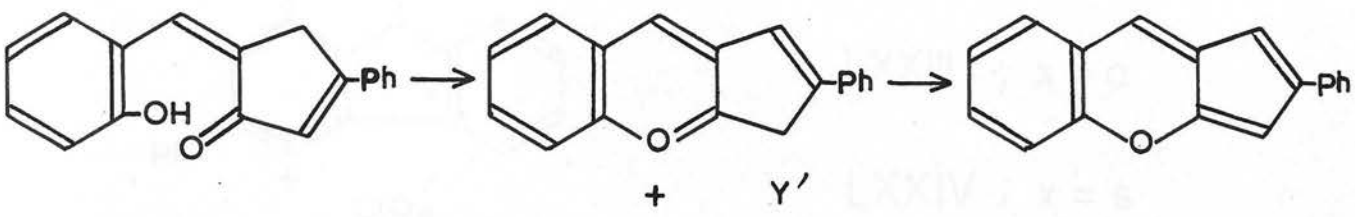
Two basic processes have been developed:

(1) Direct condensation of an o-hydroxyaldehyde with a substance containing the group CH_2CO, usually in ether or acetic acid, by means of dry hydrogen chloride.

If the reaction is carried out in the presence of perchloric acid, a stable perchlorate can often be isolated (Le Fèvre, J., 1933, 1532).

(2) Condensation of the reagents in alkaline solution to an o-hydroxystyryl ketone, followed by a conversion to a pyrylium salt by the action of strong acid.

Boyd (Chem. and Ind., 1957, 1244) has prepared the oxygen analogue of XXXI, 2-phenylbenzo[b]cyclopenta[e]pyran XXXIV, employing scheme (2):

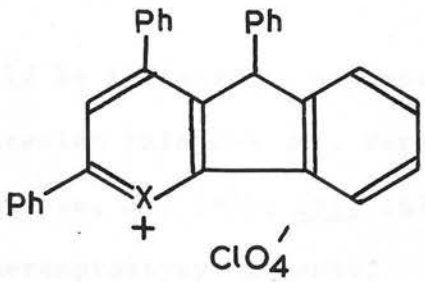


LXXII XXXIV

5-Salicylidene-3-phenylcyclopent-2-enone on treatment with acetic acid-hydrochloric acid gave a solution of the benzopyrylium chloride (LXXII; Y = Cl), which when poured into water yielded the pyran XXXIV.

Comparatively very little work has been done on the thiapyrylium salts. Wizinger and Ulrich (Helv. Chim. Acta, 1956, 39, 207) synthesized triarylthiapyrylium salts by the action of sodium sulphide on the corresponding, readily available pyrylium salts. Treatment of a triarylpyrylium salt with sodium hydroxide opens the ring with the formation of a keto-enolate, whereas with sodium sulphide a keto-thioenolate is formed; ring closure on treatment with acid splits off water and encloses the sulphur atom.

Boyd (J., 1959, 55) has applied the same reaction to 2,4,5-triphenyl-5H-indeno[1,2-b]pyrylium perchlorate LXXIII (which failed to give the anhydro-base on treatment with alkali, but suffered a ring opening to a nearly colourless pseudo-base), and obtained the corresponding thiapyrylium salt LXXIV in almost quantitative yield.



LXXIII ; X = O

LXXIV ; X = S

The latter readily lost the elements of perchloric acid to yield the thiapyran LVII. A similar procedure could not be adopted for the preparation of XXXI since the Wizinger and Ulrich reaction does not apply to the benzopyrylium salts; furthermore, 2-phenyl-3 (or 1) H-benzo[b]cyclopenta[e]-pyrylium perchlorate (LXXII; Y = Cl O_4) even on treatment with cold water yields the anhydro-base and it would thus be impossible to effect the conversion to the thiapyrylium salt.

Lüttringhaus and Engelhard (Chem. Ber., 1960, 93, 1525) reported the synthesis of the parent benzothiapyrylium salts (1- and 2-thianaphthalenium salts) from the thiachromanones, but as far as it is known there are no recorded attempts to prepare benzothiapyrylium salts by replacing salicylaldehyde by o-mercaptobenzaldehyde in the standard condensations employed in the synthesis of the pyrylium salts.

Several attempts were made to condense o-mercaptobenzaldehyde with 3-phenyl or 3,4-diphenylcyclopent-2-enones (the latter was prepared by the method of Geissman and Koelsch, J. Org. Chem., 1939, 3, 498). Application of Le Fèvre's (loc. cit.) pyrylium salt synthesis yielded deep red solutions with greenish fluorescence but there was no deposition of solid and on subsequent working up of the solution no useful product

could be isolated. Attempted condensations in methanolic potassium hydroxide solution (cf. Borsche and Menz, 1908, 41, 202; Pratt and Robinson, J., 1922, 121, 1577) also failed to give the required o-mercaptostyryl ketones.

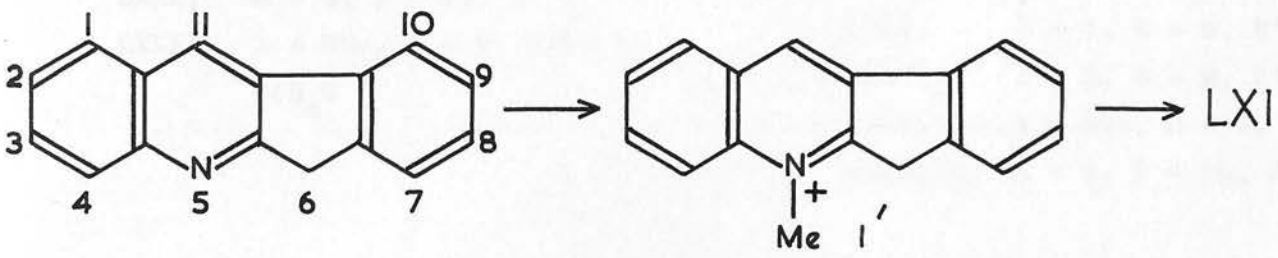
The condensation of o-mercaptobenzaldehyde and acetophenone was then attempted, both to study the conditions necessary for the possible synthesis of 2-phenylbenzothiapyrylium salt and to serve as a model for the eventual preparation of 2-phenyl-3 (or 1) H-benzo[b]-cyclopenta[e]-thiapyrylium salt. Application of Le Fèvre's synthesis did not give the required product and instead, when the reaction was carried out in acetic acid medium, dilution of the reaction mixture with water resulted in isolation of a brilliant blue dye. It was obtained as an amorphous powder which was soluble in organic solvents and stable under weakly acidic conditions, but its acetic acid solution turned colourless on addition of alkali or concentrated hydrochloric acid and the blue colour was only restored on partial neutralisation. The blue sulphur compound (which was only formed in presence of oxygen) was analysed but no satisfactory structure could be suggested.

Numerous attempts have been made to condense acetophenone and o-mercaptobenzaldehyde to the thiasalicylidene derivative. Alkaline media of different strengths were employed and to avoid possible oxidation of o-mercaptobenzaldehyde to the corresponding disulphide, nitrogen was passed through the solution during the reflux, but the required product was not formed. When the reactions were carried out under more strongly

alkaline conditions, only acetophenone and some yellow resin, which was presumed to be polymerised o-mercaptobenzaldehyde, could be isolated; under milder conditions acetophenone and traces of unpolymerised o-mercaptobenzaldehyde were recovered and identified as their 2,4-dinitrophenylhydrazones.

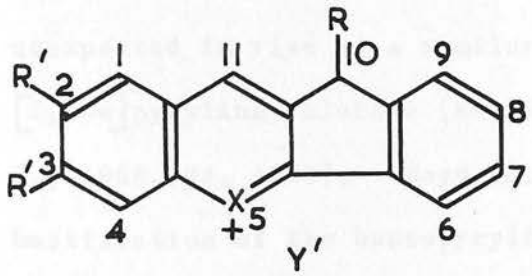
The failure of the attempts to use o-mercaptobenzaldehyde in the thiapyrylium salt synthesis can probably be attributed to the polymerisation of the aldehyde under the acidic or alkaline conditions required for the synthesis.

Having accomplished the synthesis of benzo[b]indeno[1,2-e]-thiapyran XXXII, attention was then turned to the analogous nitrogen compound, 5-methylindeno[2,1-b]quinoline LXI. The white, crystalline 6H-indeno[2,1-b]quinoline was prepared by acid condensation of o-amino-benzaldehyde and indan-2-one, followed by basification (Clemo and Felton, J., 1952, 1658). Quaternisation with methyl iodide gave the yellow methiodide which on treatment with sodium carbonate, ammonium hydroxide or hot water very readily lost the elements of hydrogen iodide to form the purple-violet anhydro-base LXI.



This pseudoazulene was very unstable and could not be recrystallised to a sharp melting point; it was therefore characterised as its trinitrobenzene derivative, which was considerably more stable than the parent compound. The solutions of LXI in mineral acids were pale yellow and like those of the nitrogen pseudoazulenes XLIV - XLVII exhibited a brilliant blue fluorescence. Since this preparation of LXI, Treibs and Schroth (Angew. Chem., 1959, 71, 578) also reported its synthesis but gave no experimental details.

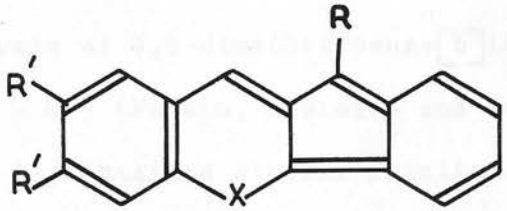
The synthesis of compound LXI completed the tetracyclic series of the analogous nitrogen, sulphur and oxygen pseudoazulenes (Table VII). Attempts were then made to synthesise a second tetracyclic series, consisting of compounds LXXV, LXXVI, and LXXVII, which like pseudoazulenes XXI and LIII - LX, possess the unfavourable o-quinonoid ring in their covalent canonical forms.



LXXIX; X = O, R = H, R' = H

LXXX; X = O, R = Ph, R' = H

LXXXI; X = NMe, R = H, R'R' = OCH_2O



XXI; X = NMe, R = Ph, R'R' = OCH_2O

LXXV; X = O, R = H, R' = H

LXXVI; X = S, R = H, R' = H

LXXVII; X = NMe, R = H, R' =

LXXVIII; X = O, R = Ph, R' = H

The pseudoazulenes with quinonoid structures are known to be either very unstable or else apparently incapable of existence, but they can be stabilised by aromatic groups and, e.g., the nitrogen compound XXI required the presence of a phenyl substituent in the five-membered ring for its formation. It was therefore realised that great difficulty would be encountered in the synthesis of compounds LXXV - LXXVII, but several attempts were made because it would be of particular interest to compare their absorption spectra with those of the analogous pseudoazulenes of the already completed tetracyclic series.

Benzo[b]indeno[2,1-e]pyrylium perchlorate (LXXIX; Y = ClO_4) was prepared by condensation of salicylaldehyde and indan-1-one in the presence of hydrogen chloride and perchloric acid (cf. Le Fèvre, loc cit.). On hydrolysis with base it did not yield the pseudoazulene LXXV, but instead suffered ring opening to 2-salicylideneindan-1-one, a result not unexpected in view of a similar hydrolysis of 7,8-dimethoxybenzo[b]indeno-[2,1-e]pyrylium chloride (as LXXIX; Y = Cl) (Perkin, Robinson and Turner, J., 1908, 93, 1085). Boyd (J., 1959, 55) obtained similar results on basification of the benzopyrylium tetrachloroferrate (LXXIX; Y = $FeCl_4$). He also examined the 10-phenylbenzopyrylium salt LXXX in the hope that the phenyl substituent might stabilise the benzoindenopyran system. The action of sodium hydroxide or sodium acetate on this salt again caused hydrolysis to the salicylidene compound, rather than the formation of the anhydro-base LXXVIII.

The reactions of the benzopyrylium perchlorate (LXXIX; Y = ClO_4) were further investigated; treatment with a hot solution of sodium acetate in acetic acid, followed by pouring of the reaction mixture into water, resulted in isolation of a basic, purple-violet solid. It was unstable and was particularly susceptible to atmospheric oxidation and sunlight: the purple-violet colour of solutions in organic solvents, while stable for several hours in an atmosphere of nitrogen and in darkness, faded in under one hour on exposure to the air and light. The solid, however, could be kept for much longer periods.

The purple-violet solid was degraded by alumina; it was obtained in the form of an amorphous powder and could not be crystallised to a sharp melting point. Its absorption spectrum differs from that of the tetracyclic oxygen pseudoazulene XXXV and from the spectra of the pseudoazulenes with quinonoid structures synthesised by Boyd (LIII - LVII) in that it shows only one intense band (and one very slight inflexion) in the ultraviolet region (Fig.7 ; "B").

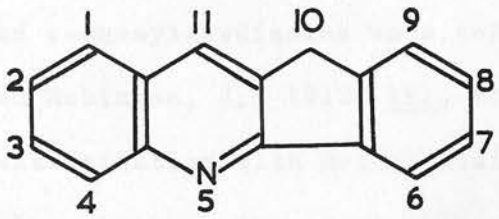
Pseudoazulene LXXV would possess an unfavourable o-quinonoid ring in its covalent canonical forms and its diplor forms should therefore be of greater relative importance than those of the isomeric pseudoazulene XXXV. Thus if the purple-violet compound was the pseudoazulene LXXV, it would be expected to be more basic than the Kekulé-type analogue XXXV. In fact it appeared to be less basic (Ho ($K' = 1$) = -5.32; Fig. 3, "B") and its acid solutions exhibited a pale blue fluorescence (within a range, decreasing in intensity with the increase in acid concentration), quite

unlike the intense greenish-yellow fluorescence of the pyrylium salts.

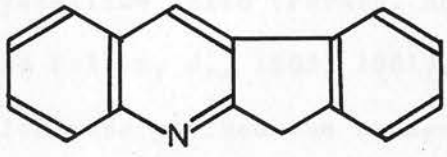
The purple-violet compound is therefore probably not the pseudoazulene LXXV, but may rather be its oxidative dimer, which would be expected to be more stable than the monomeric compound. In the absence of reliable analytical data, all conclusions must be tentative, but the above would be in agreement with Boyd's (loc. cit.) evidence that even the phenyl substituted pseudoazulene LXXVIII could not be prepared.

Attempted condensation of indan-1-one and o-mercaptobenzaldehyde, in the presence of piperidine acetate, failed to give the pseudoazulene LXXVI; benzene or alcoholic solutions remained yellow after reflux and did not fluoresce on addition of acid.

Attempts to synthesise the nitrogen pseudoazulene LXXVII also failed. The colourless crystalline 10H-indeno[1,2-b]-quinoline hydrochloride was prepared by the acid condensation of o-aminobenzaldehyde and indan-1-one. On treatment with hot, dilute sodium hydroxide solution it gave a colourless free base LXXXII which exhibited an intense fluorescence in solution.



LXXXII



LXXXIII

Ruhemann and Levy (J., 1913, 103, 563) prepared LXXXII by alkaline condensation when it was obtained together with o-aminobenzylidene-indanone.

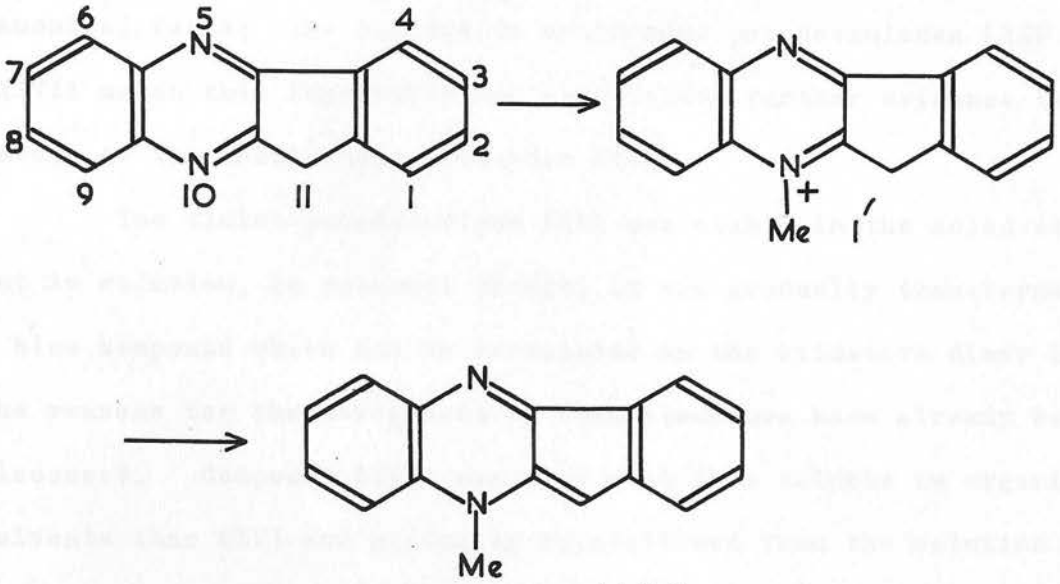
10H-Indeno[1,2-b]quinoline LXXXII, unlike its (2,1-b) isomer LXXXIII, could not be N-methylated with methyl iodide. This may be due to the electron-withdrawing character of the right-hand side benzene ring, which in the latter compound is separated from position 2 of the quinoline nucleus by a methylene group, while in the former (LXXXII) it would tend to make the nitrogen lone pair of electrons less available to electrophilic attack.

The crystalline methosulphate, however, formed quite readily, but on treatment with basic reagents it did not give pseudoazulene LXXVII, a result not unexpected in view of a similar failure to convert 2,3-methylenedioxy-5-methyl-10H-indeno[1,2-b]-quinolinium methosulphate (LXXXI; Y = Me SO_4) to the corresponding pseudoazulene (as XXI, R = H) (Armit and Robinson, J., 1922, 121, 827.)

Attention was next turned to the "pseudoaza-azulenes", in order to study the effect of replacing the CH group of the six-membered hetero-ring of the pseudoazulene by an atom of nitrogen.

11H-Indeno[1,2-b]quinoxaline was prepared from indan-1,2-dione and o-phenylenediamine as a colourless, crystalline solid (Perkin, Roberts and Robinson, J., 1912, 101, 234; Clemo and Felton, J., 1952, 1661). Quaternisation with methyl iodide in a sealed tube yielded the orange salt, which on treatment with sodium carbonate, ammonium hydroxide, or

hot water readily lost the elements of hydrogen iodide to form a deep violet anhydro-base LXVI.



LXVI

The violet pseudoazulene can be assigned the 10-methyl structure LXVI on the following evidence. The methylating agent is expected to attack $N_{(10)}$, in preference to $N_{(5)}$, for the same reasons as those given to explain the difficulty encountered in quaternisation with methyl iodide of LXXXII, which was in marked contrast to the very ready N-methylation of the isomeric indeno[2,1-b]-quinoline LXXXIII. The more forcing conditions required for the N-methylation of the analogous indenoquinoxaline are in agreement with the fact that the quinoxalines are normally more difficult to quaternise than the quinolines, and can

be accounted for by the electron-attracting character of the second nitrogen atom.

If methylation occurred at $N_{(5)}$, the violet pseudoazulene would possess an unfavourable o-quinonoid ring in its covalent canonical forms; the failure to synthesise pseudoazulenes LXXV - LXXVII makes this improbable and constitutes further evidence in favour of the Kekulé-type structure LXVI.

The violet pseudoazulene LXVI was stable in the solid state, but in solution, in presence of air, it was gradually transformed to a blue compound which can be formulated as the oxidative dimer LXVII; the reasons for the assignment of this structure have already been discussed. Compound LXVII was very much less soluble in organic solvents than LXVI and gradually crystallised from the solution of the latter in long, dark blue needles.

A small proportion of LXVII is normally present in the crude LXVI and chromatography on alumina fails to produce a clean separation of the blue and violet zones. The efficient separation of the two compounds can, however, be achieved as a result of the difference in their basicities. Compound LXVI is much more basic and can be completely removed by extraction with 10% hydrochloric acid, while LXVII remains in the organic phase. The violet anhydro-base is regenerated on basification of the aqueous extract.

As a result of the rapid oxidative dimerisation of LXVI, purification by recrystallisation is not very satisfactory. Fortunately

only LXVI reacts with 2,4,7-trinitrofluorenone to give a crystalline molecular complex which is considerably more stable than the uncomplexed pseudoazulene. Its stability in solution depends on the solvent, the temperature, and the presence or absence of oxygen and light. After several weeks in a stoppered vessel in darkness, very slight transformation to LXVII was observed only in the alcoholic solution, but none in benzene, which remained unaltered after several months (R.T.). Sunlight accelerates the transformation to LXVII, but it also causes a more rapid decomposition of the pseudoazulene, the colour of the solution turning from violet to green; thus removal of the solvent after long exposure yields impure LXVII.

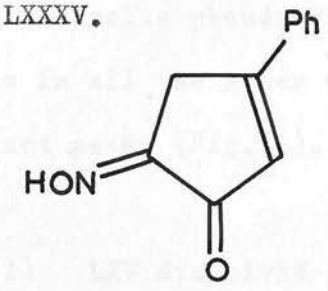
The acid solutions of LXVI were yellow and exhibited a brilliant, pale blue, fluorescence. In contrast, the oxidative dimer LXVII dissolved in mineral acids without any fluorescence; it also appeared considerably less basic (Ho ($K' = 1$) = -2.55, against +0.28 for LXVI) and the slope of its straight line plot of log K' against Ho was steeper than that of LXVI (approximately 3 and 1 respectively; Fig. 4). The oxidative dimer also differed from the monomeric pseudoazulene in its great stability: its solutions remained unaltered after several weeks in an open vessel and were unaffected by sunlight.

The absorption spectra of the two compounds are similar, but the visible band of the oxidative dimer LXVII has higher extinction coefficients and is divided into two flat maxima, while that of the monomer LXVI shows

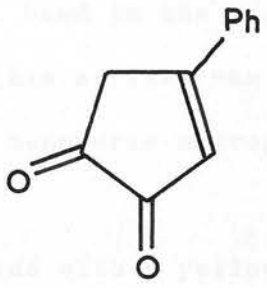
only one maximum. In the near-ultraviolet region a discreet maximum of LXVI is replaced in LXVII by an inflexion (Figs. 9,13).

The nitrogen pseudoaza-azulene, 2-phenyl-4-methylcyclopenta[b]-quinoxaline LXV, was then prepared in order to examine the effect of a second hetero-atom on the properties of the tricyclic pseudoazulenes.

Nitrosation of 3-phenylcyclopent-2-en-1-one led to the expected hydroxyimino compound LXXXIV which was then hydrolysed, in the presence of formaldehyde as a hydroxylamine acceptor, to the yellow crystalline diketone LXXXV.



LXXXIV



LXXXV

Geissman and Koelsch (J. Org. Chem., 1939, 3, 489) obtained 1,5-diphenyl-cyclopent-1-en-3,4-dione by analogous reactions but better results were obtained by adopting essentially the same procedure as used by Perkin, Roberts and Robinson (J., 1912, 101, 234) for the preparation of indan-1,2-dione.

The diketone LXXV readily condensed with o-phenylenediamine to a colourless, crystalline 2-phenyl-1 (or 3) H-cyclopenta[b] quinoxaline, which on quaternisation with methyl iodide in a sealed tube yielded a reddish salt. Treatment of the methiodide with ammonium hydroxide gave

a blue, crystalline anhydro-base LXV.

The pseudoaza-azulene was more stable than the analogous cyclopenta[b]quinoline XLIV, but like all the monomeric nitrogen pseudoazulenes, it was very susceptible to atmospheric oxidation and sunlight. Unlike its tetracyclic analogue LXVI, it did not form an oxidative dimer and its solutions, in the presence of air, gradually faded to pale yellow.

The absorption spectrum of LXV very closely resembled those of the other tricyclic pseudoazulenes and its band in the near-ultraviolet region, as in all the other compounds in this series, was split into two distinct peaks (Fig. 8). Like other monomeric nitrogen pseudoazulenes -

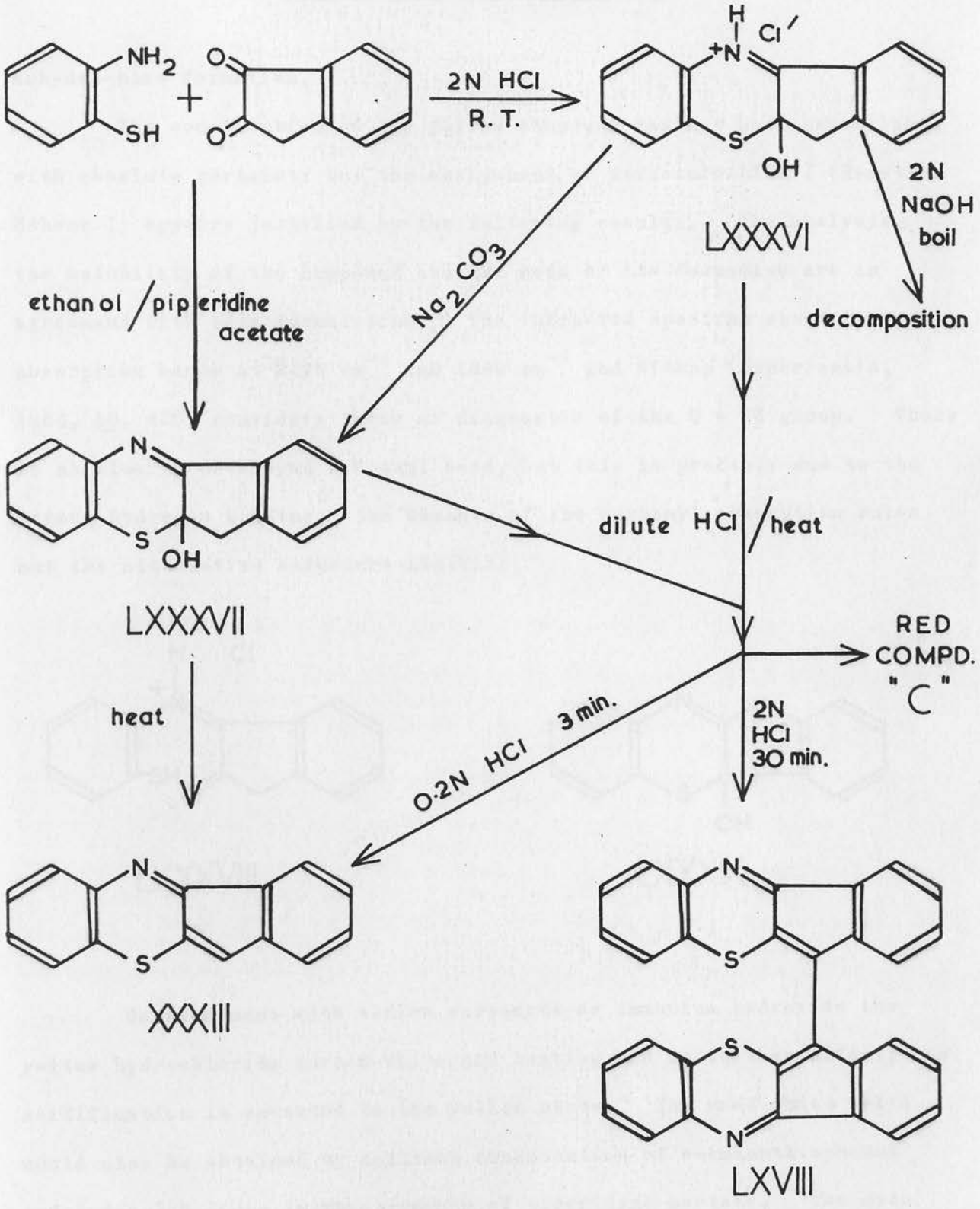
(1) LXV dissolved in mineral acids with a yellow colour and blue fluorescence;

(2) it readily formed molecular complexes with trinitrobenzene and trinitrofluorenone;

(3) the slope of its linear "basicity" plot of log K' against Ho approximated to one (Fig. 1).

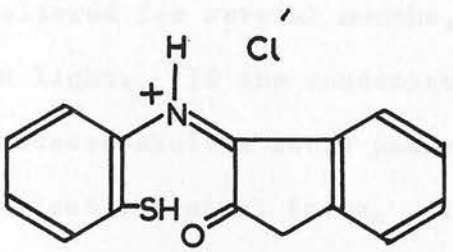
Attention was next turned to the synthesis of the sulphur pseudoaza-azulenes. Several attempts were made to condense o-aminothiophenol and indan-1,2-dione in different media. Condensation in dilute hydrochloric acid in the cold yielded a yellow crystalline hydrochloride. It was practically insoluble in non-polar solvents, but readily dissolved in boiling alcohol with a reddish colour, indicating

REACTION SCHEME I

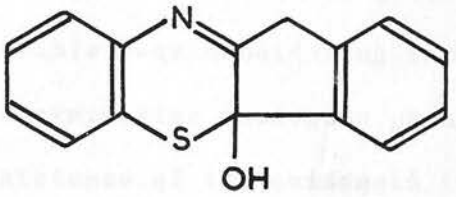


anhydro-base formation.

The constitution of the yellow compound has not been established with absolute certainty but the assignment of structure LXXXVI (Reaction Scheme I) appears justified by the following results. The analysis, the solubility of the compound and the mode of its formation are in agreement with this formulation. The infra-red spectrum shows two absorption bands at 2495 cm^{-1} and 1890 cm^{-1} and Witkop (Experientia, 1954, 10, 420) considers these as diagnostic of the $C = \overset{+}{N}H$ group. There is no clearly developed hydroxyl band, but this is probably due to the strong hydrogen bonding; the absence of the carbonyl absorption rules out the alternative structure LXXXVIII.



LXXXVIII



LXXXIX

On treatment with sodium carbonate or ammonium hydroxide the yellow hydrochloride turned white and heating had no further effect; on acidification it reverted to the yellow state. The same white solid could also be obtained by a direct condensation of o-aminothiophenol and indan-1,2-dione in the presence of piperidine acetate. The mode

of its formation and the analysis indicate that the white compound is the free pseudo base. The closed ring structure is again confirmed by the infra-red spectrum which shows a weak hydroxyl band at 3620cm^{-1} and no carbonyl adsorption. Two such structures, however, are possible, depending on whether the amino or the mercapto group of o-aminothiophenol condenses with the β-carbonyl group of indan-1,2-dione. The pseudo-base can be formulated as LXXXVII (Reaction Scheme I), in preference to LXXXIX, on the following evidence.

At higher temperatures the white compound very readily lost the elements of water to yield a dark red pseudoaza-azulene. The latter appeared indefinitely stable in the solid state and, in solution, remained unaltered for several months, provided it was kept in absence of oxygen and light. If the condensation had yielded pseudo-base LXXXIX, the red pseudoaza-azulene would possess an unfavourable o-quinonoid ring in its covalent canonical forms. The failure to synthesise analogous pseudo-azulenes LXXV - LXXVII and the fleeting existence of the quinonoid indeno-[1,2-b]thiapyran LVII make this improbable and constitute evidence in favour of the Kekulé structure XXXIII for the sulphur pseudoaza-azulene and of structures LXXXVI and LXXXVII for the hydrochloride and the free pseudo-base respectively.

The formulation of the sulphur pseudoaza-azulene as XXXIII is confirmed by comparison with the nitrogen pseudoaza-azulene ~~comparison~~ which was assigned the analogous

Kekulé structure LXVI. The two compounds are formally identical in all respects save in the nature of the hetero-atom replacing the -CH = CH- grouping of azulene. In agreement with the orders of the wavelengths of the visible absorption maxima (λ max.), basicities, and stabilities in the analogous nitrogen and sulphur pseudoazulenes possessing Kekulé structures, (Tables VII and VIII) -

(1) The nitrogen pseudoaza-azulene LXVI absorbed at longer wavelength in the visible region than the sulphur analogue XXXIII (λ max. = 579 mμ and 519 mμ respectively).

(2) Compound LXVI appeared considerably more basic than XXXIII (Ho (K' = 1) = +0.28 and -2.65, respectively).

(3) The sulphur pseudoaza-azulene crystallised in beautiful long needles and was considerably more stable than the nitrogen analogue, which showed greater sensitivity to light and oxygen and, although obtained in a crystalline state, did not melt sharply and was characterised as its trinitro-fluorenone complex.

An alternative method of preparing pseudoaza-azulene XXXIII involved heating of the hydrochloride LXXXVI (or the free pseudo-base LXXXVII) in dilute hydrochloric acid (the reaction must be carried out in acidic medium, for in boiling water the hydrochloride is largely

converted to the free pseudo-base and anhydro-base formation is very restricted). Purification of the crude material by chromatography on alumina resulted in isolation, in addition to XXXIII, of two other basic compounds, (one violet and the other red). The violet compound can be formulated as the oxidative dimer LXVIII; the assignment of this structure has been previously discussed. The red compound was always formed only in a trace quantity, but the relative proportions of XXXIII and LXVIII depended on the concentration of the acid, the period of heating, and the presence or absence of oxygen. Pseudoaza-azulene XXXIII was best prepared in dilute acid (ca. 0.2 N hydrochloric acid) with a short period of boiling (3 minutes), followed by a rapid cooling; similar results were obtained by carrying out the reaction under nitrogen. On the other hand, the preparation of the oxidative dimer in a good yield required a more concentrated acid (2N HCl) and an increase in the period of heating. Prolonged refluxing of the hydro-chloride LXXXVI in 2N acid under nitrogen yielded mostly the unchanged reactant, together with a small quantity of XXXIII and only a trace of LXVIII (probably due to incomplete removal of oxygen). The formation of the latter compound only in the presence of oxygen is consistent with structure LXVIII.

The preferential formation of the oxidative dimer in 2N acid (in the presence of oxygen) can be related to its lesser basicity. In the more strongly acidic reaction medium, the equilibrium between the pseudoazulene and its salt (as XXVI) will show a greater shift in favour

of the former in a less basic compound; therefore the oxidative dimer LXVIII can accumulate to a greater extent than XXXIII by a continual oxidation of the latter.

The absorption spectra of XXXIII and LXVIII were very similar but, as in the analogous nitrogen pseudoaza-azulenes (LXVI and LXVII), the oxidative dimer (LXVIII) showed higher extinction coefficients and its visible band was divided into two flat maxima, while that of the monomer (XXXIII) showed only one maximum. In both sulphur compounds, however, the near-ultraviolet band was sharper than in the nitrogen analogues and was segmented into two distinct peaks (Fig. 10).

Both the oxidative dimers LXVII and LXVIII were very much less soluble in organic solvents than the monomers LXVI and XXXIII. The slopes of the linear plots of Log K' against Ho of LXVII and LXVIII were almost identical and both were steeper than those of the corresponding monomers LXVI and XXXIII (Fig. 4).

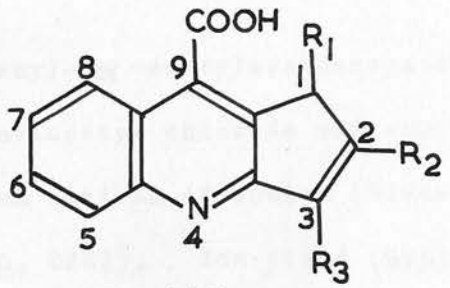
The similarity between the nitrogen and the sulphur oxidative dimers is consistent with their analogous structures LXVII and LXVIII.

The third basic compound ("Red Compound C"; Reaction Scheme I) isolated from the crude material obtained by boiling LXXXVI in dilute hydrochloric acid, was only present in a trace quantity and was not examined in detail. It dissolved in mineral acids with a green colour (XXXIII and LXVIII dissolved with yellow and yellow-green colour, respectively) and was regenerated on basification. The presence of chlorine, the mode of its formation, and the apparent similarity of its

basicity to that of XXXIII suggested that the red compound could be a chloro derivative of XXXIII, but the one analysis for chlorine was not in agreement with either the mono- or the di-chloro compound; no alternative structure could be suggested.

Los and Stafford (J., 1959, 1680) synthesised a number of phenyl substituted pseudoazulenes of the cyclopenta[b]quinoline series (XLIV - XLVII) and examined their absorption spectra. In order to investigate further the possibility of molecular overcrowding in certain members of this series, it was desired to synthesise two additional compounds: XLVIII and XLIX.

Borsche (Ann., 1910, 377, 120; Ber., 1908, 41, 2203) prepared 2,3-dihydro-1H-cyclopenta[b]quinoline from cyclopentanone by the Pfitzinger reaction with subsequent decarboxylation of the resulting 9-carboxylic acid. Los and Stafford failed to effect its dehydrogenation but were able to obtain the desired system in the form of more complex derivatives by a direct alkaline condensation of isatin and substituted cyclopent-2-en-1-ones. The resulting acid XC could then be decarboxylated and the pseudoazulene prepared by quaternisation with methyl iodide, followed by basification with sodium carbonate.



XC

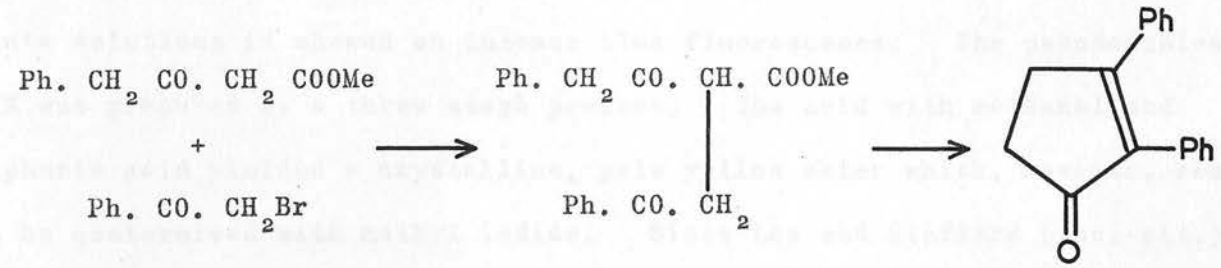
Treatment of XC with diazomethane yielded the corresponding 9-carbomethoxy pseudoazulene which could also be prepared by successive esterification, N-methylation and basification.

Treibs and Kempter (Chem. Ber., 1959, 92, 601) have also investigated the synthesis of pseudoazulenes of the cyclopenta[b]quinoline series, but their approach differed from that of Los and Stafford, for no attempts were made to effect direct dehydrogenation of 2,3-dihydrocyclopenta[b]-quinolines. Instead, N-methylation with dimethyl sulphate represented the first stage in the synthesis, followed by treatment with alkali and dehydrogenation as the final stage. They were successful in the synthesis of only one pseudoazulene, 3-phenyl-4,9-dimethylcyclopenta[b]quinoline L; the presence of the phenyl group is important since attempts to prepare the unsubstituted compound failed.

The preparation of 2,3-diphenylcyclopent-2-en-1-one represented the initial stage in the synthesis of the required pseudoazulenes XLVIII and XLIX. The original synthesis of the ketone is due to Borsche and Klein (Ber., 1939, 72B, 2082). This was repeated but the yields were low and it was necessary to introduce certain modifications to obtain better results.

Ethyl γ-phenyl-α-acetylacetoacetate was prepared by the condensation of phenylacetyl chloride and ethyl acetoacetate in the presence of magnesium instead of sodium (Viscontini and Merckling, Helv. Chim. Acta, 1952, 35, 2280). The yield (89%) and the quality of the

product were much better than those obtained by the older methods (Sonn and Litten, Ber., 1933, 66B, 1512; Metzner, Ann., 1897, 298, 374). A number of attempts were then made to discover the best conditions for the saponification of the α-acetyl compound to the β-keto ester. Treatment with 0.5% aqueous ammonia (Sonn and Litten, loc. cit.) gave a very low yield of γ-phenylaceto-acetate and better results were obtained by using 5% ethanolic ammonia and following the procedure adopted by Viscontini and Adank (Helv. Chim. Acta, 1952, 35, 1342) for the preparation of ethyl benzoylacetate (51% yield). The simplest and the best method, however, was that of Hunsdiecker (Ber., 1942, 75, 454), the α-acetyl group being removed by the action of sodium methoxide at R.T. (71%).



The condensation of the sodium salt of the β-ketoester and phenacyl bromide was best carried out in ether, under essentially the same conditions as used by Weidlich and Daniels (Ber., 1939, 72B, 1590) for the preparation of ethyl γ-methyl-α-phenacylacetoacetate. The cyclisation (and the decarboxylation) of the derivatives of α-phenacylacetoacetic

esters to the corresponding cyclopent-2-enones was described by Borsche and co-workers (Ber., 1939, 72B, 2082; 1908, 41, 194; 1906, 39, 1922) Weidlich and Daniels (loc. cit.) and Winternitz, Mousseron and Rouzier (Bull. Soc. chim., 1953, 196). All the authors used analogous methods which, however, varied in certain experimental details and best yields (65-72%) of 2,3-diphenylcyclopent-2-en-1-one were obtained by the method of Winternitz et al., which involved heating of the ester in 5% aqueous sodium hydroxide in a stream of nitrogen.

The ketone condensed smoothly with isatin in ethanolic potassium hydroxide to 2,3-diphenylcyclopenta[b]quinoline-9-carboxylic acid (XC; R_1 = H, R_2 = R_3 = Ph). The acid was very sparingly soluble in most organic solvents and crystallised with difficulty (best from benzene); in dilute solutions it showed an intense blue fluorescence. The pseudoazulene XLIX was prepared by a three stage process. The acid with methanol and sulphuric acid yielded a crystalline, pale yellow ester which, however, could not be quaternised with methyl iodide. Since Los and Stafford (loc. cit.) had no difficulty in preparing the analogous 2-phenyl and 1,2-diphenyl methiodides, the difficulty encountered with the 2,3-diphenyl compound may be due to the steric effect of the phenyl group at $C_{(3)}$. N-Methylation was only achieved after prolonged reflux with a large excess of dimethyl sulphate in benzene. The methosulphate was not isolated but was converted directly to the anhydro-base by extraction into dilute acetic acid, followed by basification with sodium carbonate. The deep blue pseudoazulene XLIX was crystalline and appeared indefinitely stable in the solid state.

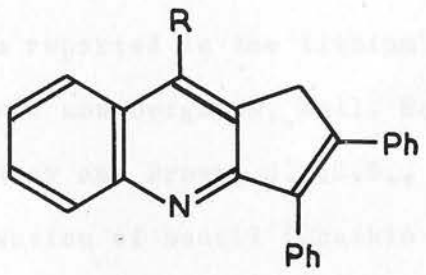
Los and Stafford encountered difficulties in the decarboxylation of the 2-phenyl and the 1,2-diphenyl acids (as XC) and could only prepare very small quantities of the corresponding cyclopenta[b]quinolines by dry distillation with soda lime under reduced pressure. Both compounds were very unstable and only the diphenyl compound could be obtained pure. One of the standard procedures to effect decarboxylation consists of heating the acid in quinoline in the presence of copper bronze. When this was applied to 2,3-diphenylcyclopenta[b]quinoline-9-carboxylic acid, (as XC) the solution became brilliant red, and, following the removal of quinoline by steam distillation, chromatography on alumina separated two products: a dark red solid of unknown structure (λ max. in ethanol, 500, 315 and 243 mμ) and a golden-yellow crystalline solid, which analysed correctly for 2,3-diphenyl-9-hydroxycyclopenta[b]quinoline, but was not further investigated.

The replacement of a carboxylic acid by a hydroxyl group in the analogous position in the quinoline nucleus has been reported by Buu-Hoï and Royer (J., 1948, 106). They found that in many instances dry distillation of 2-alkylcinchoninic acids, without alkaline catalysts, afforded not only the expected 2-alkylquinolines, through decarboxylation, but also the corresponding 4-hydroxy-2-alkylquinolines by the loss of carbon monoxide. Dry distillation of acid (XC; R_1 = H, R_2 = R_3 = Ph), however, failed to give useful products.

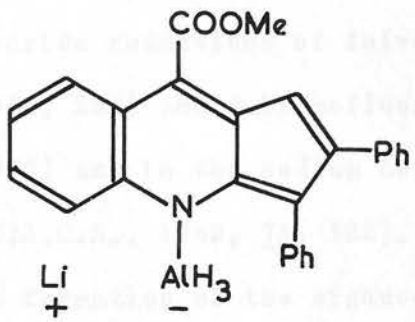
Pyrolysis in the presence of soda lime yielded a mixture of products. Chromatography on alumina showed the presence of two fluorescing

compounds. The pale blue fluorescing 2,3-diphenylcyclopenta[b]quinoline was unstable and could not be obtained pure; it was directly converted to the methosulphate which on treatment with sodium carbonate gave a mauve anhydro-base XLVIII, characterised as its trinitrobenzene complex. The second product of the pyrolysis was a stable golden-yellow solid which melted to a red oil and in dilute solutions showed a striking violet-blue fluorescence, but was not further investigated. Analysis indicated the presence of oxygen.

Several attempts were made to reduce 2,3-diphenyl-9-carbomethoxy-cyclopenta-[b]quinoline (XCI; R = COOMe) with lithium aluminium hydride to the corresponding hydroxymethyl compound (XCI; R = CH_2OH).



XCI



XCII

Although the attempted reductions were carried out in the presence of a large excess of the hydride and for long periods, only the unreacted ester was isolated. When ether was used as solvent the recovery of the ester was almost quantitative, but in tetrahydrofuran there was considerable decomposition of the reactant during refluxing and only a small amount

of the ester could be recovered after a troublesome purification.

Addition of a few drops of the ester solution to the concentrated refluxing solution of the hydride always caused the formation of a brilliant purple coloration. The coloured compound was very unstable and decomposed almost immediately in the presence of air; the purple colour could be maintained by addition of the ester at a constant rate but when this ceased the solution turned pale yellow.

The purple colour formed equally readily in the cold and after its disappearance it could not be restored on heating. In the absence of air the coloured compound remained stable for a few hours and it was therefore possible to obtain a qualitative absorption spectrum (Fig. 12).

The formation of brightly coloured organo-metallic products has been reported in the lithium aluminium hydride reductions of fulvenes (Lavie and Bergmann, Bull. Soc. chim., 1951, 250) and 9-bromofluorene (Trevoy and Brown, J.A.C.S., 1949, 71, 1677) and in the sodium borohydride reduction of benzil (Chaikin and Brown, J.A.C.S., 1949, 71, 122). Lavie and Bergmann attributed the colour to the formation of the organo-alkali metal complex Ar - C - Li (and not Ar - C - Al, which would be colourless, cf. Hochstein and Brown, J.A.C.S., 1948, 70, 3484), indicating that it was lithium hydride which was the effective reducing agent.

The reddish coloured compounds formed during the reduction of fulvenes appeared quite stable and were only destroyed by the addition of water, while in the reduction of 9-bromofluorene an orange colour appeared on the first addition of the halide, disappeared as the reaction

progressed, and reappeared after its completion. As far as is known, the appearance of coloured products has never been reported in the reduction of esters and there does not appear any possibility for the formation of an analogous organo-metallic compound during the attempted reduction of XCI (R = COOMe).

Structure XCII is tentatively suggested for the purple compound; it is analogous to the structure of the blue pseudoazulene XLIX, the N-methyl group being replaced by aluminium hydride. The absorption spectra of the two compounds are given in Fig. 12: a quantitative comparison is not possible but their general similarity is consistent with structure XCII.

The formulation of the purple compound as XCII appears in agreement with theories of the lithium aluminium hydride reduction mechanism. Trevoy and Brown (J.A.C.S., 1949, 71, 1675) concluded from a wide range of evidence that the rate determining step is a bimolecular nucleophilic substitution by a hydride ion, possibly complex. Paddock (Nature, 1951, 167, 1070; Chem. and Ind., 1953, 63) examined the role of solvent in the reduction and has shown that the analogy between lithium aluminium hydride and the Grignard reagent extends to the necessity for a donor solvent. It is considered that in solution there is an equilibrium -

$$Al H_4' \rightleftharpoons H' + Al H_3$$

and that for reduction to occur, a solvent possessing electron-releasing properties must be present, for it can co-ordinate with aluminium hydride and drive the equilibrium to the right-hand side. This function is usually performed by ether, but other electron-donors may also be used, e.g., tetrahydrofuran, and in certain instances even acetone or benzonitrile.

It is suggested that the ester (XCI; R = COOMe) could also act as an electron donor, the nitrogen lone pair of electrons co-ordinating with aluminium hydride; the purple pseudoazulene is then obtained by removal of the proton by a hydride ion.

Following the synthesis of 2,3-diphenyl-4-methylcyclopenta[b]-quinoline XLVIII, attention was turned to the analogous oxygen pseudoazulene XXXVII. 2,3-Diphenylcyclopent-2-enone condensed with salicylaldehyde in ethanolic sodium hydroxide to a pale yellow crystalline salicylidene derivative (cf. Borsche and Menz, Ber., 1908, 41, 202), which could also be obtained by boiling an ethanolic solution of the reactants in the presence of piperidine acetate. Cyclisation to 2,3-diphenylbenzo[b]cyclopenta[e]pyran XXXVII was achieved by heating the salicylidene compound in acetic acid-hydrochloric acid. Boyd (J., 1958, 1978) and Los and Stafford (J., 1959, 1680) reported the synthesis of the 2-phenyl and the 1,2-diphenyl derivatives XXXIV and XXXVI respectively, by analogous reactions and in almost quantitative yields. In contrast, XXXVII was obtained in a poor yield and its purification was only achieved after

repeated chromatography on alumina.

In view of the successful syntheses of the 1H-cyclopenta[b]-quinoline derivatives (as XLIII) by the condensation of isatin and the corresponding cyclopent-2-enones, attempts were made to condense the latter with thianaphthenequinone and coumaran-2,3-dione respectively.

Thianaphthenequinone was prepared by a ring closure reaction of thiophenol and oxalyl chloride (Stolle, Ber., 1914, 47, 1130; Papa, Schwenk and Ginsberg, J. Org. Chem., 1949, 14, 723). The attempted condensation with 3,4-diphenylcyclopent-2-enone in alcoholic potassium hydroxide yielded a yellow amorphous solid which failed to react with hydrochloric acid-perchloric acid. Treatment with hydrogen chloride in dry methanol caused the appearance of a transient red coloration, but only the unchanged reactant was isolated. The infra-red spectrum and the analysis also indicated that the yellow solid could not be the thiosalicylidene derivative, but was probably a polymer.

The attempted alkaline condensation of 3,4-diphenylcyclopent-2-enone and coumaran-2,3-dione (Huntress and Hearon, J.A.C.S., 1941, 63, 2763) also failed and only the reactants were isolated.

Absorption Spectra

The wavelengths and $\log_{10} E$ values of the visible and ultraviolet absorption maxima of pseudoazulenes and certain other compounds, whose preparation and properties have been described, are listed in Table XII (Figs. 5-13).

TABLE XII

Compound [a]	$\lambda_{max.}$ (mμ)	$\log_{10} E^{Molar}_{1\ cm.}$
2-Phenylbenzo[b]cyclopenta[e]thiapyran XXXI (Fig. 5)	520 406 385 368 278 265	2.77 4.08 4.26 4.18 4.41 4.40
Benzo[b]indeno[1,2-e]thiapyran XXXII (Fig. 6).	500 366 350 334 299 292	3.36 3.94 4.04 3.99 4.71 4.71
Benzo[b]indeno[1,2-e]-[1,4]-thiazine XXXIII (Fig. 10).	519 374 357 292 257 250	3.35 3.97 4.07 4.66 4.37 4.35
Di(benzo[b]indeno[1,2-e]-[1,4]-thiazin-11-yl[b] LXVIII (Fig. 10).	572 514 381 365 299 276	3.75 3.73 4.45 4.43 4.69 4.69

(continued)

Compound(a)	$\lambda_{max.}$ (mμ)	$Log_{10} E^{Molar}_{1\ cm.}$
5-Methylindeno[2,1-b]quinoline LXI T.N.B. (Fig. 6).	531 355 320* 298	3.44 3.91 4.37 4.82
5-Methylindeno[2,1-b]quinoline LXI (Fig. 13)	534 355* 320* 298	3.35 3.81 4.34 4.61
2-Phenyl-4-methylcyclopenta[b]-quinoxaline LXV T.N.B. (Fig. 8)	599 413 392 283	3.01 4.45 4.52 4.64
2-Phenyl-4-methylcyclopenta[b]-quinoxaline LXV	599 412 392 283	3.00 4.43 4.51 4.62
10-Methylindeno[2,1-b]quinoxaline LXVI T.N.F. (Fig. 9)	579 349 290	3.36 4.22 4.91
10-Methylindeno[2,1-b]quinoxaline LXVI (Fig. 13)	579 352 297	3.32 3.88 4.69
Di(10-methylindeno[2,1-b]-quinoxalin-11-yl) LXVII (Fig. 9)	610 411 362* 307	3.67 3.39 4.18 4.89

(continued)

Compound[a]	$\lambda_{max.}$ (mμ)	$\log_{10} E^{Molar}_{1\ cm}$
2,3-Diphenyl-4-methylcyclopenta-[b]quinoline XLVIII T.N.B. (Fig. 11).	533 370 298 242	3.10 4.09 4.44 4.31
2,3-Diphenylbenzo[b]cyclopenta-[e]pyran XXXVII (Fig. 11)	510 362 256	2.89 4.43 4.59
2,3-Diphenyl-4-methyl-9-carbomethoxycyclopenta[b] quinoline XLIX T.N.B. (Fig. 12)	574 378 305 249 243	3.02 4.20 4.49 4.30 4.29
		$\log_{10} E^{1\%}_{1cm}$
"Blue compound A" T.N.F. (Fig. 7)	617 355* 290	1.74 2.69 3.01
"Purple compound B" (Fig. 7)	531 315* 282	1.71 2.13 2.43
2-Phenyl-4-methylcyclopenta-[b]-quinoline XLIV[cc]	536 395 375 292	

(continued)

Compound[a]	$\lambda_{max.}$ ($m\mu$)	$\log_{10} E^{Molar}_{1\ cm}$
"Purple compound" formed by addition of $LiAlH_4$ to solution of 2,3-diphenyl-9-carbomethoxycyclopenta [b]quinoline (Fig. 12)[b]	542 355 303 266 256 250	

(a) Unless stated otherwise the solvent was ethanol.

(b) In tetrahydrofuran

(c) In benzene

* Inflexion.

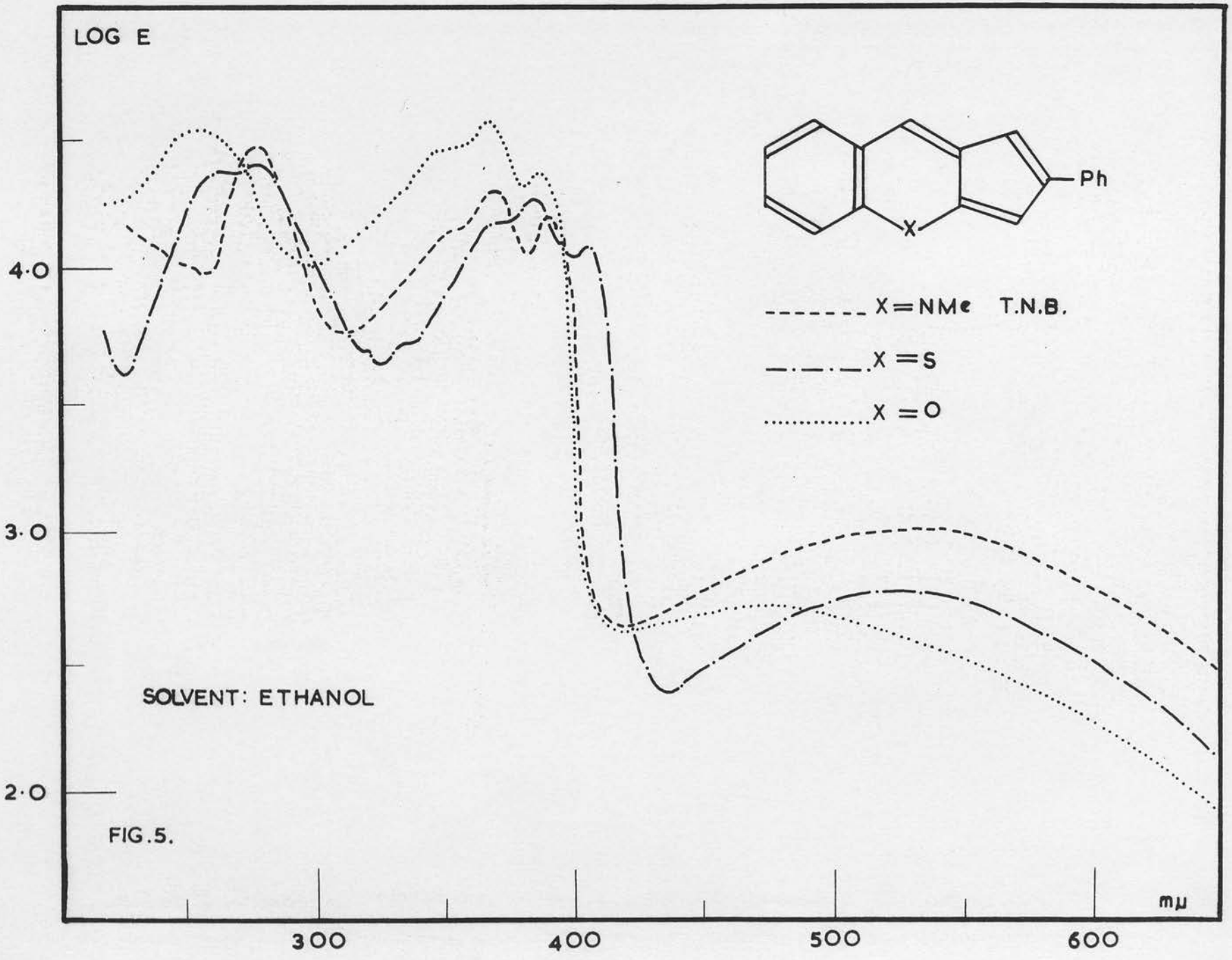

LOG E
4·0
3·0
2·0
Ph
X
X=NMe T.N.B.
X=S
X=O
SOLVENT: ETHANOL
300
400
500
600
mμ

FIG.5.

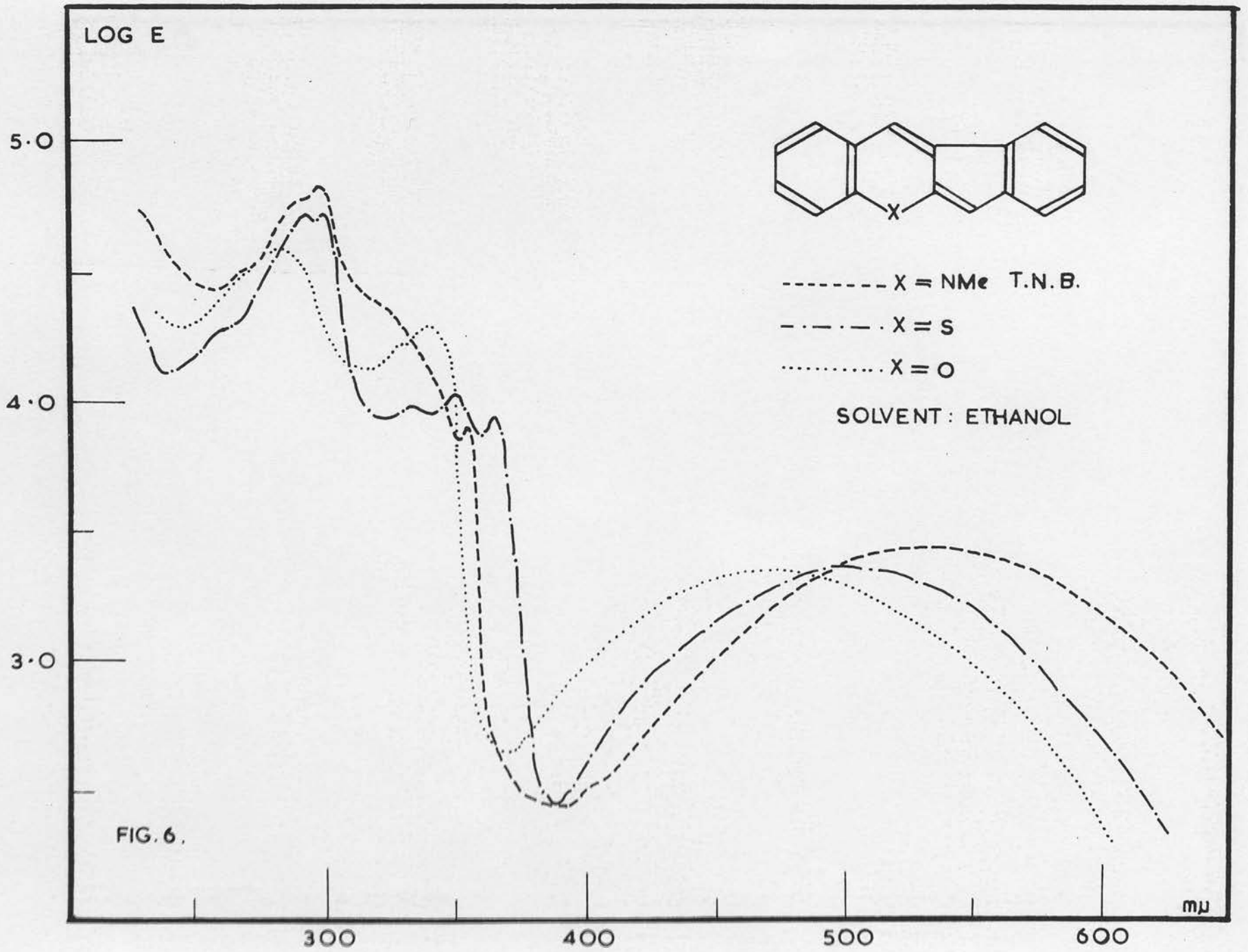

LOG E
5·0
4·0
3·0
X
X = NMe T.N.B.
X = S
X = O
SOLVENT : ETHANOL
300
400
500
600
mμ

FIG. 6.

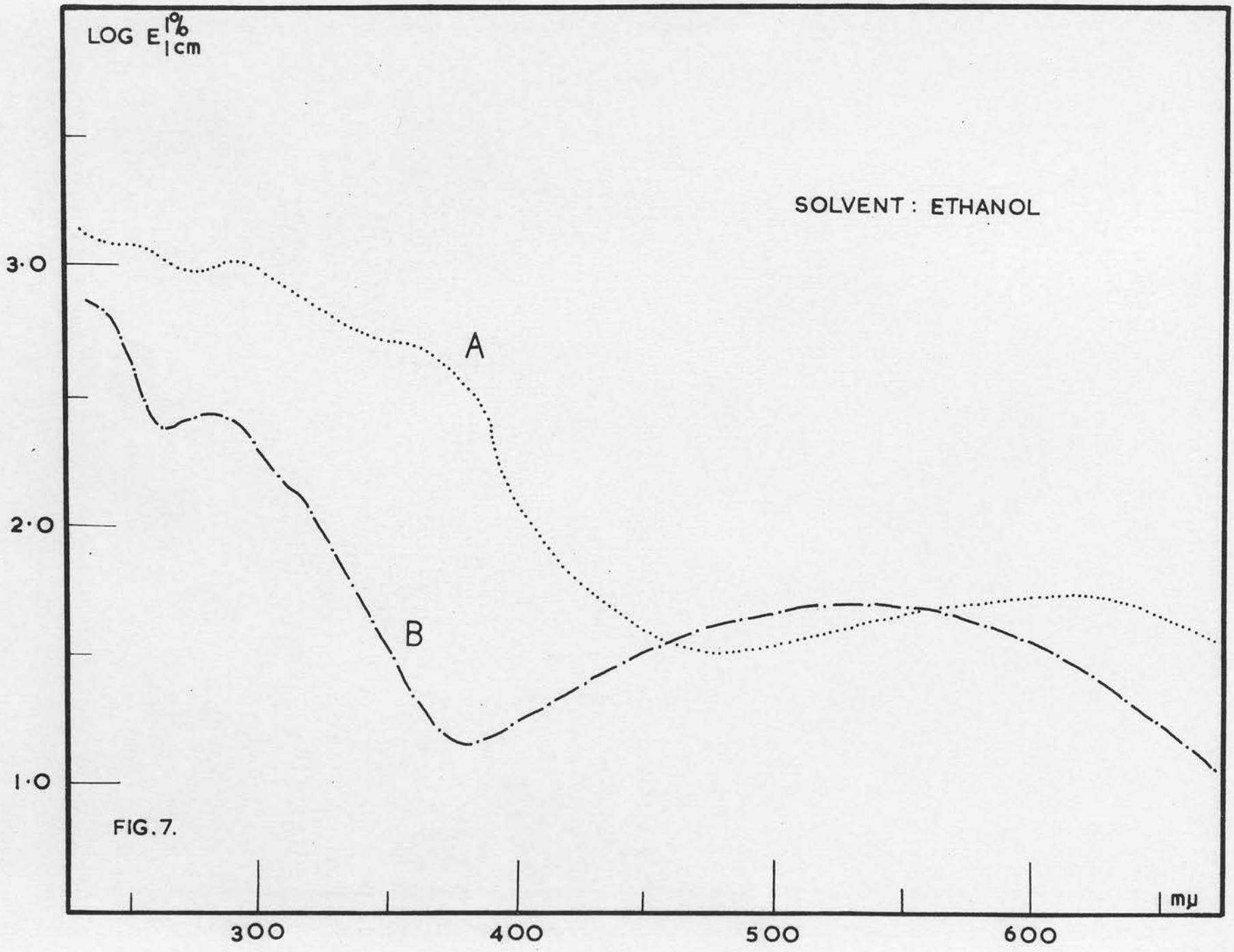


FIG. 7.

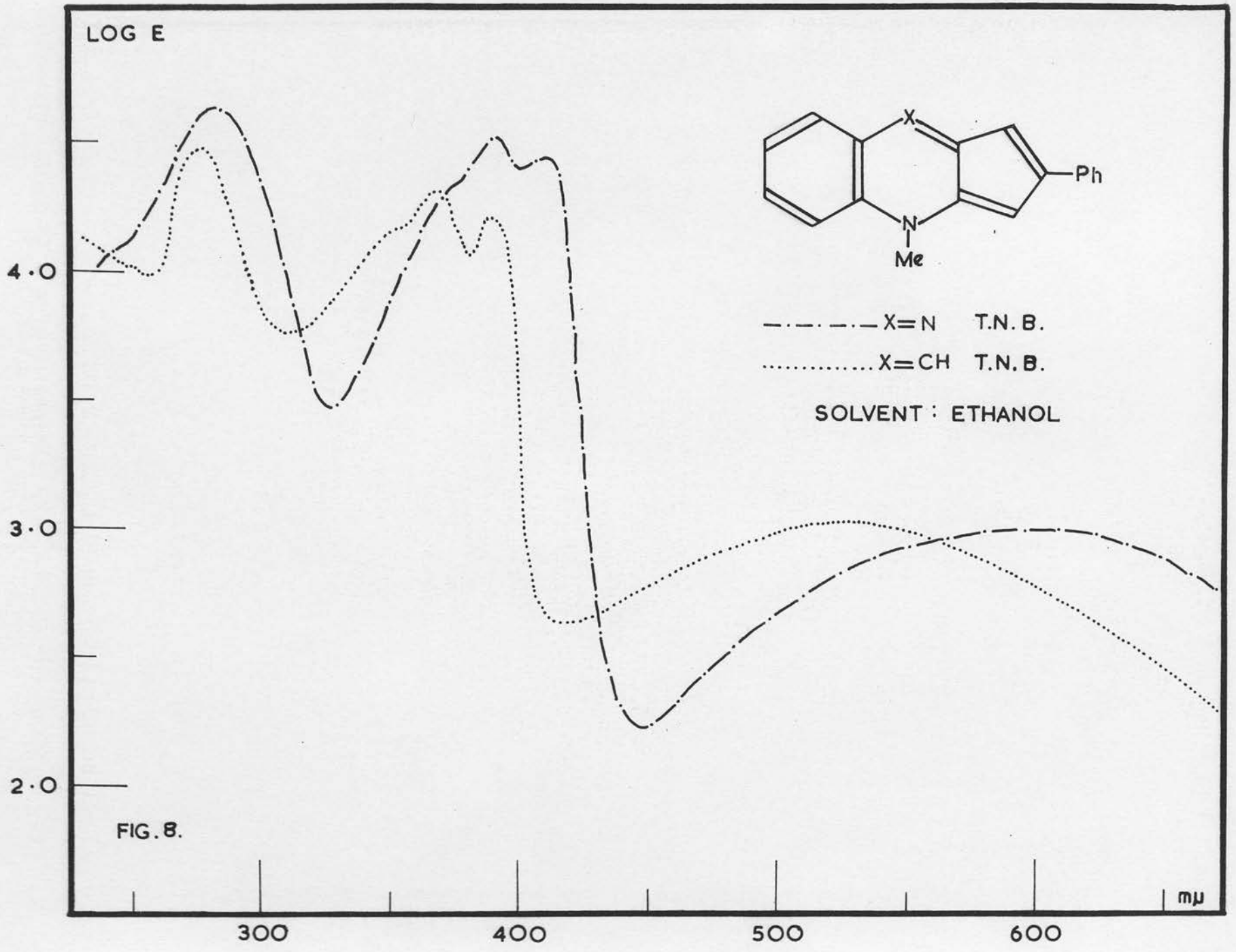

LOG E
4·0
3·0
2·0
X
Ph
N
Me
X=N T.N.B.
X=CH T.N.B.
SOLVENT : ETHANOL
300
400
500
600
mμ

FIG. 8.

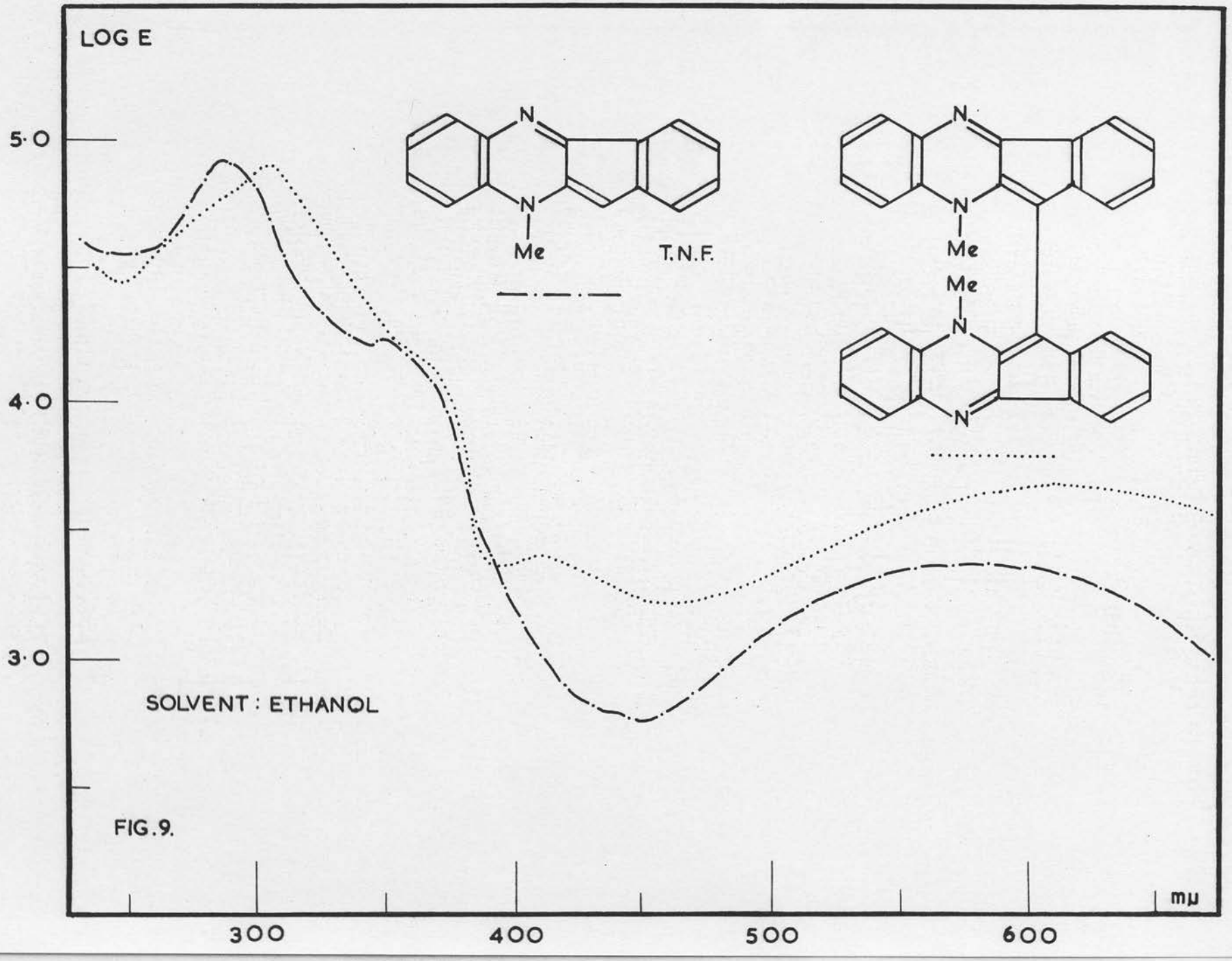

LOG E
5·0
4·0
3·0
N
N
Me
T.N.F.
N
N
Me
Me
N
N
SOLVENT : ETHANOL
300
400
500
600
mμ

FIG. 9.

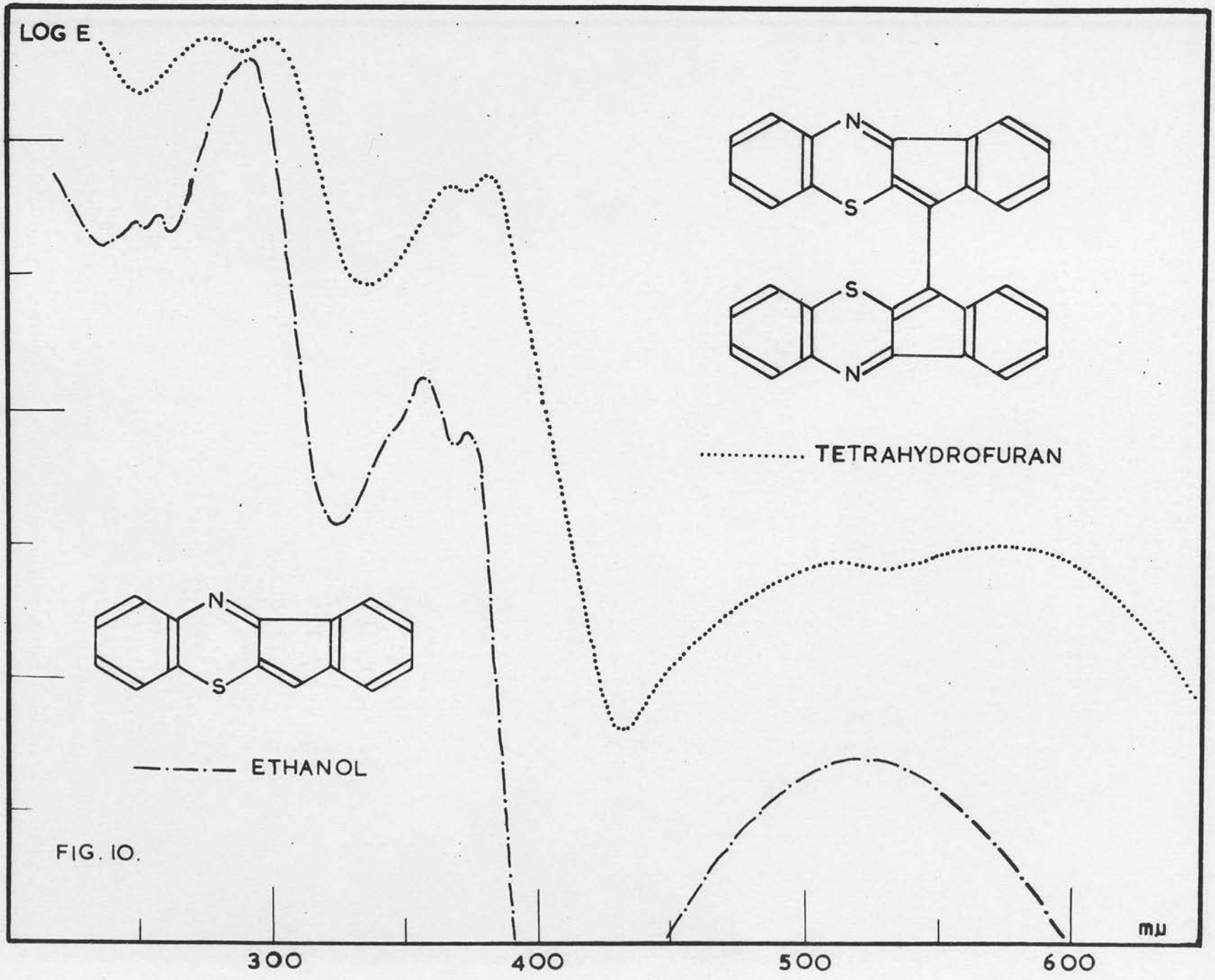

LOG E
4·5
4·0
3·5
N
S
S
N
TETRAHYDROFURAN
N
S
ETHANOL
300
400
500
600
mμ

FIG. 10.

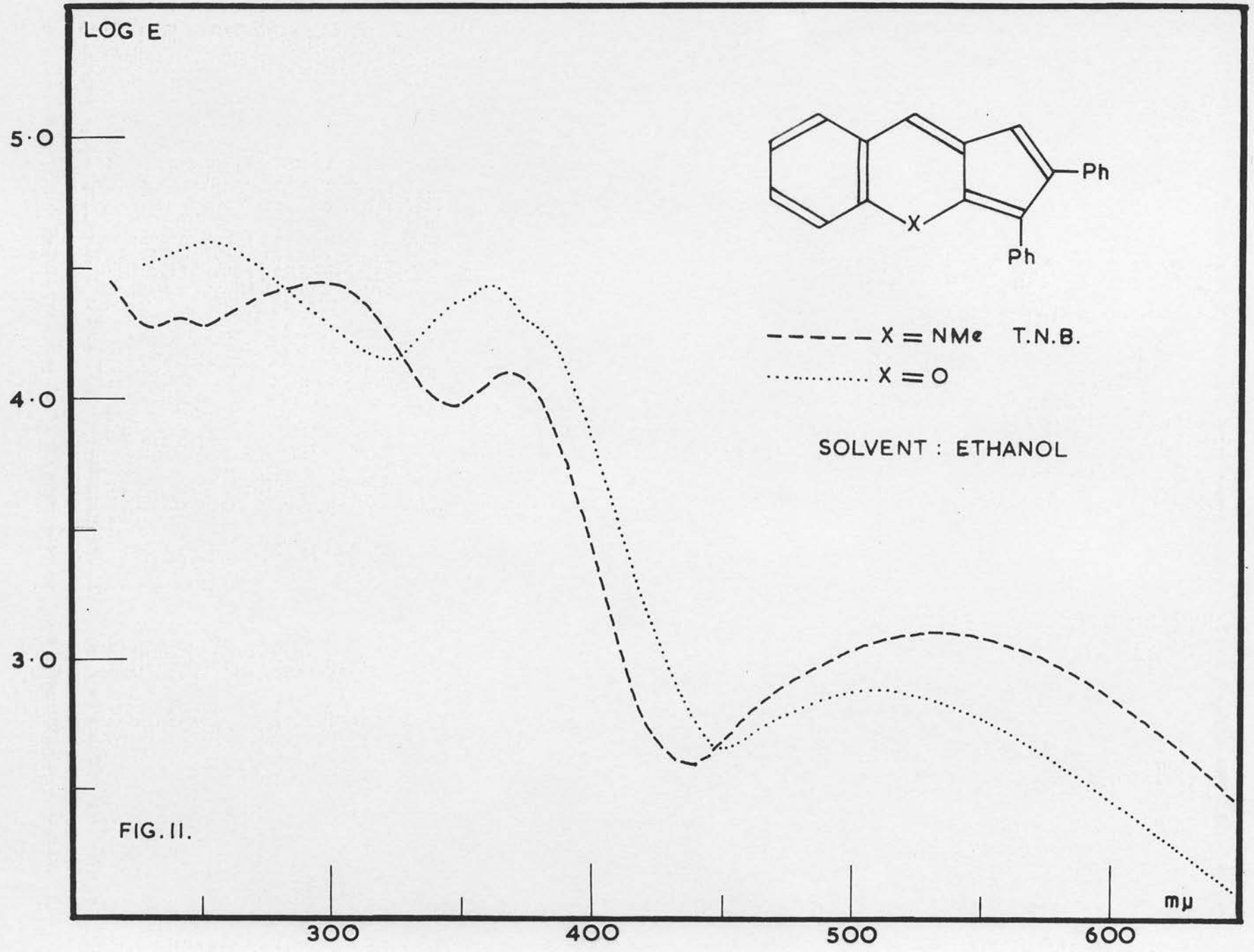

LOG E
5·0
4·0
3·0
Ph
X
Ph
X = NMe T.N.B.
X = O
SOLVENT : ETHANOL
300
400
500
600
mμ

FIG. II.

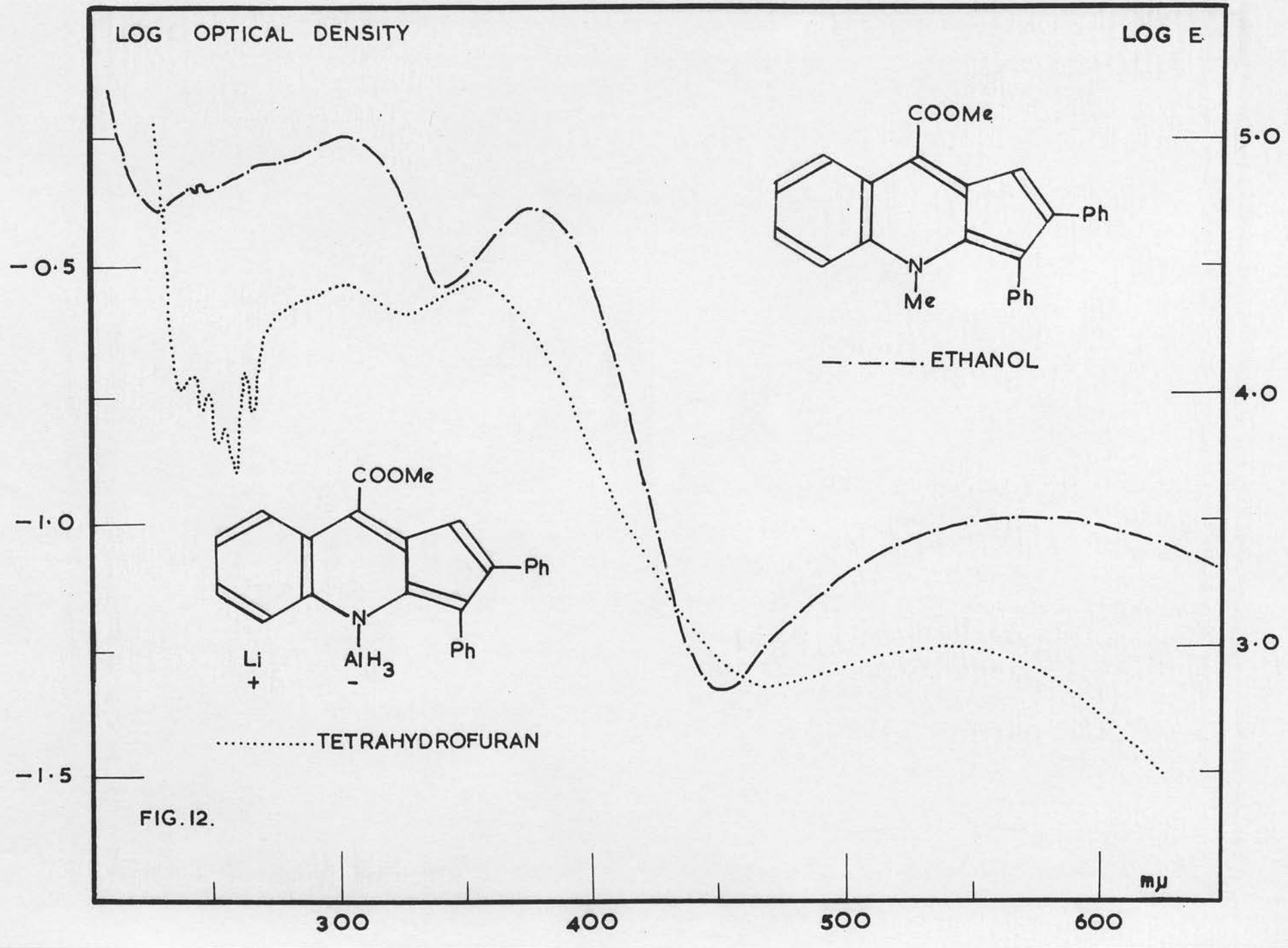

LOG OPTICAL DENSITY
LOG E
-0·5
-1·0
-1·5
5·0
4·0
3·0
COOMe
Ph
N
Me
Ph
——·——·——. ETHANOL
COOMe
Ph
N
Li
+
AlH3
-
Ph
..... TETRAHYDROFURAN
300
400
500
600
mμ

FIG. 12.

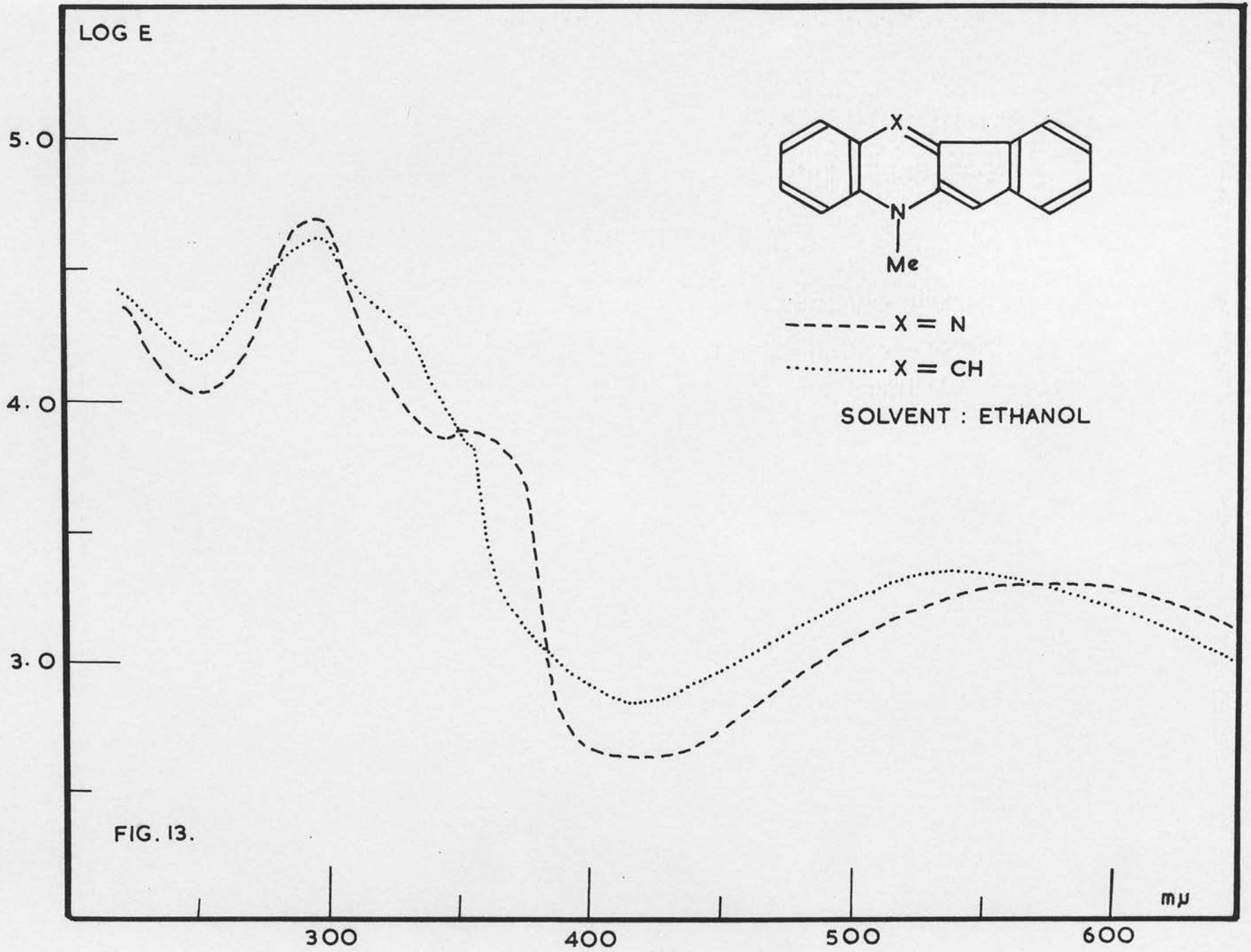


FIG. 13.

E X P E R I M E N T A L

Experimental.

All melting points were determined by means of a Kofler micro-melting point apparatus.

Chromatographic separations were carried out on columns prepared from Activated Alumina Type "H", supplied by P. Spence and Sons Ltd., Widnes.

The ultraviolet and visible absorption spectra were determined using a Unicam SP 500 spectrophotometer and 10 mm silica cells. The infra-red spectra were determined by Mr. L. Duncan and Mr. N. King.

Dr. Wilson of Glasgow University measured, by means of mass spectrometry, the molecular weights of certain of the compounds discussed (LXVII and LXVIII).

Compounds XXXVI and XLIV - XLVII were supplied by (the late) Dr. W.H. Stafford and Dr. M. Los.

Analyses were by Drs. Weiler and Strauss, Oxford.

Preparation of diphenyl disulphide 2,2'-dicarboxylic acid chloride. ("dithiosalicyl chloride")

Reissert and Manns, Ber., 1928, 61, 1312.

Diphenyl disulphide 2,2'-dicarboxylic acid ("dithiosalicylic acid") (40 g) and freshly distilled thionyl chloride (77 ml) were heated on a water bath until the evolution of hydrogen chloride ceased (6 hours). The thick, cream coloured suspension of the acid gradually changed to a pale brown solution of the chloride. When the reaction was complete, excess thionyl chloride was removed by distillation with benzene. The brownish solid residue was recrystallised from benzene, with silica gel screening, as colourless prisms, m.p. 155° (lit. m.p. 153°). Yield: 36 g, 80%.

Preparation of diphenyl disulphide 2,2'-dicarboxylic acid di-N-methylanilide.

A solution of dithiosalicyl chloride (32 g) in benzene (1200 ml) was cooled in ice while N-methylaniline (24 g, corresponding to 1.2 mole per acid chloride group) in an equal volume of pyridine was added dropwise, with shaking. To complete the reaction, the solution was refluxed for one hour. Dilute hydrochloric acid was then added and the benzene extract washed with water and dried over anhydrous sodium sulphate. Removal of the solvent gave a pale yellow viscous oil which did not crystallise (45 g). A sample of the material was purified by chromatography on alumina and crystallised from methanol as thick, colourless prismatic needles, m.p. 141 - 2°. The bulk of the product was used without further purification

for the preparation of N-(o-mercaptobenzoyl)-N-methylaniline.

Preparation of N-(o-mercaptobenzoyl)-N-methylaniline.

A solution of the foregoing N-methyl anilide (40 g) in glacial acetic acid (400 ml) was heated to boiling in a strong current of carbon dioxide. Zinc dust (12 g) was gradually introduced to the refluxing solution over a period of three hours. The solution was then filtered and a small sample tested with an aqueous solution of sodium nitroprusside, when a red colouration and precipitate indicated the presence of a free mercapto group. The anilide was isolated by addition of water (1000 ml) and immediate extraction with ether (3 x 500 ml). The combined ether extracts were washed with sodium carbonate solution, (until free from acetic acid,) and water and dried over anhydrous sodium sulphate. The solvent was removed in a current of carbon dioxide and the anilide obtained as a very pale yellow crystalline solid (33 g, 82%) with characteristic mercaptan smell. Recrystallisation from petrol ether (b.p. 80-100°) gave colourless prisms, m.p. 92-93°. Weygand et al. (Angew. Chem., 1953, 65, 525), who prepared the anilide from o-mercaptobenzoic acid, give m.p. 85°.

Analysis Found: C, 69.1; H, 5.5; N, 5.8; S, 13.0

$C_{14}H_{13}NOS$ requires: C, 69.1; H, 5.4; N, 5.8; S, 13.2

Preparation of o-mercaptobenzaldehyde

cf. Weygand et al., Angew. Chem., 1953, 65, 525.

A solution of N-(o-mercaptobenzoyl)-N-methylaniline (26 g) in

tetrahydrofuran (150 ml), which had been dried with lithium aluminium hydride, was cooled in an ice-salt mixture and a solution of lithium aluminium hydride (3.0 g, corresponding to 0.5 m. of hydride per methylanilide group +0.25 m. per mercapto group) in dry ether (300 ml) was added dropwise with stirring over a period of 45 minutes. The rate of addition of the hydride must be such that the temperature of the reaction mixture does not rise above 0^{o}. The solution soon became bright yellow, but at the end of addition it was yellowish-green. The stirring was continued for 18 hours at 0^{o}. The excess hydride was then destroyed by introduction of small pieces of ice; the solution became brilliant orange and a copious white precipitate formed. A clear, pale yellow solution was obtained after dropwise addition of 0.05 N hydrochloric acid (300 ml). More ether was then added and the extract was thoroughly washed with water and dried over anhydrous sodium sulphate.

Because of its instability, o-mercaptobenzaldehyde could not be purified by steam distillation. Removal of the solvent from a portion of the solution yielded a pale yellow oil, which rapidly resinified on exposure to the air. The rest of the aldehyde was kept in solution at 0^{o} and remained unaltered for several weeks. The yield was estimated by preparing its 2,4-dinitrophenylhydrazone from one tenth of the original volume of solution (2.0 g, 60%). Recrystallisation from glacial acetic acid gave orange crystals, m.p. 269-270^{o} (with sublimation). Weygand et al gave m.p. 269^{o}.

Analysis Found: C, 49.2; H, 3.3; N, 17.3

$C_{13}H_{10}N_4O_4S$ requires: C, 49.05; H, 3.1; N, 17.6

Preparation of indan-2-one

Pope and Read, J., 1912, 101, 760; Read and Hurst, J., 1922, 121, 2554.

Indene (20 g) gave 2-bromo-3-hydroxyindane (29 g) which was used for the preparation of indan-2-one. It was obtained as a colourless solid (24 g) which crystallised from ethanol in long needles, m.p. 57-58° (lit. m.p. 58°).

Preparation of benzo[b]indeno[1,2-e]thiapyran

Indan-2-one (0.9 g) and o-mercaptobenzaldehyde (0.9 g) in ethanol (20 ml), in the presence of a small quantity of piperidine acetate, were boiled under reflux for 30 minutes. The solution soon became deep red. On cooling a dark reddish-brown solid crystallised; it was filtered and washed with a little ethanol. Ethanol was distilled from the filtrate and the residue taken up in benzene and filtered through an alumina column. Removal of solvent yielded more crystalline pyran; total yield 1.2 g. It was recrystallised from ethanol in beautiful leaf-like plates, which appeared copper coloured in mass, but reddish by transmitted light, m.p. 209-209.5°.

Analysis

Found: C, 82.4; H, 4.3; S, 13.1

$C_{16}H_{10}S$ requires: C, 82.0; H, 4.3; S, 13.6

Preparation of 3-phenylcyclopent-2-en-1-one.

Winternitz, Mousseron and Rouzier, Bull. Soc. chim., 1953, 196.

Ethyl phenacylacetoacetate (58 g) gave 3-phenylcyclopent-2-en-1-one, (26 g, 70%), m.p. 79-80°. Borsche and Fels (Ber., 1906, 39, 1922) give m.p. 82-83°.

The 2,4-dinitrophenylhydrazone was prepared in the usual manner. It crystallised from glacial acetic acid in dark red prisms, m.p., 255-256°. Los (Ph.D. Thesis, Edinburgh) gives m.p. 255-257°.

Reaction of o-mercaptobenzaldehyde with 3-phenylcyclopent-2-en-1-one.

o-Mercaptobenzaldehyde (1.1 g) and 3-phenylcyclopent-2-en-1-one (1.3 g) in benzene (50 ml), in the presence of a small quantity of piperidine acetate, were boiled under reflux for 1 hr. 30 min. The solution gradually darkened, first from yellow-orange to pale brown and after 30 min to greenish and finally deep green. After concentration to about 25 ml, the solution was chromatographed on an alumina column (30 x 3 cm). Initial development with light petroleum (2)/benzene (1) gave two bands, the upper yellow and the lower blue. The latter then divided into blue and reddish-purple zones which travelled close together without distinct separation. During further development the blue zone gradually became fainter but continued to be followed by an intense reddish-purple trail.

The reddish-purple eluates were concentrated before filtration through a column (20 x 3 cm), with benzene (1)//light petroleum (1) as

developer. Evaporation of the solution to a small volume gave the crystalline 2-phenylbenzo[b]cyclopenta[e]thiapyran (52 mg) which was filtered off and washed with a little ethanol. It crystallised from ethanol in clusters of dark reddish-brown leaflets, which were reddish-purple by transmitted light, m.p. 234-235° (decomp.)

Analysis

Found: C, 82.6; H, 4.8; S, 11.7

$C_{18}H_{12}S$ requires: C, 83.0; H, 4.7; S, 12.3

Evaporation (under nitrogen) of the blue eluates yielded a viscous oil which did not crystallise. It was taken up in benzene and re-chromatographed on a column (12 x 1.5 cm). Development with light petroleum (2)/benzene (1) again revealed the presence of blue and reddish-purple zones, the intensity of the former decreasing during the elution. Concentration of the blue eluates to a small volume yielded an oil which again failed to crystallise. The 2,4,7 trinitrofluorenone complex, prepared in ethanol, crystallised in very fine, threak-like needles. It showed no definite m.p., but gradually softened over a range, with melting completed at ca. 210-212°.

Analysis

Found: C, 61.1; H, 3.7; N, 8.85.

Preparation of 2-phenylbenzo[b]cyclopenta[e]pyran

Boyd, J., 1958, 1978.

5-Salicylidene-3-phenylcyclopent-2-enone (5 g) in acetic acid

(45 ml) and concentrated hydrochloric acid (5 ml) was heated on the water bath for 30 minutes. The solution was poured into water (300 ml) and 2-phenylbenzo[b]cyclopenta[e]pyran collected in quantitative yield. Crystallisation from benzene gave reddish-purple prisms, m.p. 207-208°. (lit. m.p. 207 - 207.5°).

Preparation of benzo[b]indeno[1,2-e]pyran

Boyd, Chem. and Ind., 1957, 1244.

A solution of indan-2-one (1 g) and salicylaldehyde (0.93 g, 0.8 ml) in ethanol (10 ml) was refluxed for 30 minutes in the presence of a small amount of piperidine acetate. On cooling the vivid red solution deposited crystalline benzoindenopyran (0.85 g). It was collected and recrystallised from ethanol in orange-red prismatic needles, m.p. 185-186°. Boyd gives m.p. 176-177°.

Analysis

Found: C, 88.0; H, 4.7

$C_{16}H_{10}O$ requires: C, 88.0; H, 4.6

Preparation of benzo[b]indeno[2,1-e]pyrylium perchlorate.

cf. Le Fèvre, J., 1933, 1532.

A solution of indan-1-one (1.5 g) and salicylaldehyde (1.4 g) in anhydrous ether (40 ml) containing 72% perchloric acid (3 ml) was saturated with dry hydrogen chloride at 0°. During 24 hours at 0° the solution deposited benzoindenopyrylium perchlorate (2.6 g, 72%), which crystallised from acetic acid in reddish needles, m.p. 227-228° (decomp.).

Attempted preparation of benzo[b]indeno[2,1-e]pyran.

A solution of benzo[b]indeno[2,1-e]-pyrylium perchlorate (1 g) in hot acetic acid (30 ml) was mixed with a hot acetic acid solution of sodium acetate (4 g in 30 ml). The resulting bluish-brown solution was immediately poured into water and ice (200 ml) and the precipitated dark violet gummy solid extracted into ether. The extract was washed with water and dried in darkness over two portions of anhydrous sodium sulphate (2 hr.). The solvent was removed in a stream of nitrogen on the water bath at 50°. After addition of light petroleum to the concentrated solution, a brown-purple solid (0.5 g) deposited and was collected and washed with a little methanol. It was chromatographed on a column of alumina (12 x 3 cm) with benzene as solvent and developer. A brown, strongly adsorbed, band remained at the top of the column. During the elution the purple zone became slightly fainter, indicating that the compound was gradually degraded by alumina. The eluates were concentrated to a small volume on the water-bath at 50-60° in an atmosphere of nitrogen. After addition of a little methanol, the purple solid was deposited as an amorphous powder which could not be efficiently crystallised. A concentrated methanolic solution after standing overnight at 0° deposited a purple amorphous material which gradually softened over a range before finally melting at ca. 175 - 178°.

Analysis

Found: C, 84.4; H, 4.5

(Benzo[b]indeno[2,1-e]pyran, $C_{16}H_{10}O$ requires: C, 88.0; H, 4.6).

Preparation of 6H-indeno[2,1-b]quinoline.

cf. Clemo and Felton J., 1952, 1667

o-Aminobenzaldehyde (0.70 g) and indan-2-one (0.77 g) were heated under reflux in 2N hydrochloric acid (15 ml) for 15 minutes. The crude greyish-green hydrochloride was collected (1.5 g) and a portion recrystallised from ethanol as rosettes of thin, hair-like colourless needles, m.p. 173-174° (with sublimation and decomposition). Dilute alcoholic solutions of the hydrochloride exhibited intense blue fluorescence. It was basified with hot dilute sodium hydroxide solution and the free base collected and recrystallised from methanol (0.80 g). After sublimation it was obtained in the form of colourless prisms, m.p. 141°. Borsche (Ann., 1937, 532, 127) gives m.p. 140°; Clemo and Felton give m.p. 144°.

Preparation of the methiodide of 6H-indeno[2,1-b]quinoline

Indeno[2,1-b]quinoline (0.50 g) was dissolved in benzene (20 ml) and methyl iodide (5 ml) added. Even in the cold the solution became immediately purple indicating that rapid formation of the methiodide has been followed by conversion to the anhydro-base. Boiling under reflux was continued for 2 hours. The methiodide separated from the solution in almost quantitative yield (0.80 g) and was recrystallised from ethanol as thick, pale yellow rods, m.p. 237-238° (decomp.).

Preparation of 5-methylindeno[2,1-b]quinoline

A suspension of the methiodide (0.70 g) in 10% sodium carbonate solution was shaken with chloroform until conversion to the anhydro-base was complete (30 minutes). The purple chloroform extract was dried consecutively over two portions of anhydrous sodium sulphate (2 hr.). The solvent was removed on the water-bath at 60° in an atmosphere of nitrogen (out of direct sunlight). On addition of a little cold methanol the residue solidified to a purple-violet mass (0.38 g) which was collected and washed with more methanol. The pseudoazulene did not crystallise immediately from methanol, but after standing overnight at 0°, a dark purple crystalline mass was deposited. The solid did not melt sharply, but gradually softened over a range, with melting completed at ca. 129 - 131°.

In the solid state the pseudoazulene could be kept for long periods but in solution it decomposed more rapidly and was particularly susceptible to atmospheric oxidation and sunlight. In a stoppered vessel and in darkness purple-violet solutions remained unaltered for about a day (longer at 0°), but on exposure to sunlight and air they turned completely green in a few minutes.

The trinitrobenzene complex, prepared in ethanol, crystallised in clusters of dark purple, almost black rods which appeared purple-violet by transmitted light, m.p. 161 - 161.5°.

Analysis

Found: C, 62.0; H, 3.6; N, 12.4

$C_{23}H_{16}N_4O_6$ requires: C, 62.2; H, 3.6; N, 12.6

Preparation of 10H-indeno[1,2-b]quinoline

Cf. Clemo and Felton, J., 1952, 1667.

o-Aminobenzaldehyde (1.16 g) and indan-1-one (1.26 g) were heated under reflux in 2N hydrochloric acid (15 ml) for 20 minutes. The crude orange indeno[1,2-b]-quinoline hydrochloride (1.9 g) was collected and a portion recrystallised from ethanol as slender colourless needles, m.p. 208-210°. The hydrochloride was basified with hot dilute sodium hydroxide solution and the free base (1.2 g) collected and recrystallised from aqueous ethanol as colourless needles, m.p. 171-172°. Rehemann and Levy (J., 1913, 103, 563) give m.p. 170-171°.

In dilute solution the base exhibited an intense blue fluorescence.

Preparation of methosulphate of 10H-indeno[1,2-b]quinoline

Cf. Armit and Robinson, J., 1922, 121, 833.

10H-Indeno[1,2-b]quinoline (0.5g) was dissolved in benzene (10 ml) and excess of dimethyl sulphate added. The salt separated in almost quantitative yield from the boiling solution and was recrystallised from ethanol as thick, colourless prismatic needles, which did not melt below 330°. (Found: S, 9.8; $C_{18}H_{17}NO_4S$ requires: S, 9.35).

Alcoholic solutions of the methosulphate exhibited a striking blue fluorescence.

The salt yielded no blue or purple colour on treatment with basic reagents.

Preparation of 1-phenylcyclopent-1-en-3,4-dione

Cf. (a) Gabriel and Stelzner, Ber., 1896, 29, 2604.

(b) Perkin et al., J., 1912, 101, 232.

(a) To a cooled solution of 3-phenylcyclopent-2-en-1-one (4 g) and isoamylnitrite (4.3 g) in ethanol (25 ml), concentrated hydrochloric acid (1.2 ml) was added cautiously with shaking. The solution became warm and 4-hydroxyimino-1-phenylcyclopent-1-en-3-one was gradually deposited. The reaction was completed by heating the mixture at 50-60° for 10 minutes. The pale yellow solid (3.6 g) was then collected and washed with ethanol. It crystallised from benzene in colourless crystals, m.p. 197 - 198°.

(b) To a mixture of the hydroxyimino compound (3.0 g) and 40% aqueous formaldehyde solution (25 ml), concentrated hydrochloric acid (15 ml) was added with stirring. After heating the yellow suspension at 50 - 60° for 5 minutes, the diketone (2.1 g, 80%) was collected and washed with water. It crystallised from ethyl acetate in golden-yellow plates, m.p. 194 - 195°.

Analysis

Found:	C, 76.3;	H, 4.5
$C_{11} H_8 O_2$ requires:	C, 76.7;	H, 4.7

Preparation of 2-phenylcyclopenta[b]quinoxaline

Hot concentrated ethanolic solutions of equimolecular proportions of 1-phenylcyclopent-1-en-3,4-dione (2.0 g) and o-phenylenediamine (1.3 g) were mixed and, on cooling, 2-phenylcyclopenta[b]quinoxaline separated in an almost quantitative yield (2.5 g). It was recrystallised from ethanol as long, colourless needles, m.p. 236.5 - 237.5°.

Analysis

Found:	C, 83.4;	H, 4.9;	N, 11.5
$C_{17} H_{12} N_2$ requires	C, 83.6;	H, 4.9;	N, 11.5

Preparation of the methiodide of 2-phenylcyclopenta[b]quinoxaline

A suspension of the quinoxaline (0.9 g) in methyl iodide (20 ml) was heated in a sealed Carius tube for one hour at 80 - 85°. Heating for longer periods or at higher temperatures yielded resinified product. The crude reddish-brown methiodide was collected and purified by boiling in benzene (15 ml), followed by a rapid hot filtration. The reddish-orange crystalline solid was washed with more hot benzene (0.75 g). It was practically insoluble in benzene and sparingly soluble in chloroform, acetone and ethanol, with partial decomposition on boiling. Recrystallisation from these solvents lowers the purity of the product.

The unrecrystallised material was obtained in the form of reddish-orange prismatic needles, m.p. 240 - 241° (decomp.).

Analysis

	Found:	C, 55.2;	H, 3.8;	I, 33.3;	N, 7.2
$C_{18}H_{15}IN_2$	requires:	C, 60.0;	H, 3.9;	I, 32.9;	N, 7.25

Preparation of 2-phenyl-4-methylcyclopenta[b]quinoxaline.

The methiodide (0.50 g) was suspended in 2N aqueous ammonia solution. On shaking, the solid darkened and soon became almost black. The crude anhydro-base was filtered off and thoroughly washed with water (0.30 g). It was very soluble in all common organic solvents, giving deep blue solutions. Recrystallisation from a small volume of methanol, in an atmosphere of nitrogen (twice), yielded 2-phenyl-4-methylcyclopenta[b]quinoxaline (0.19 g) as thick, dark, prismatic needles, which were dark blue by transmitted light, m.p. 160° (decomp.)

Prolonged boiling in presence of oxygen caused decomposition of the pseudoaza-azulene. The blue solutions also soon turned green and finally yellow if exposed to strong sunlight (2-3 hours).

Analysis

	Found:	C, 83.6;	H, 5.4;	N, 10.75
$C_{18}H_{14}N_2$	requires:	C, 83.7;	H, 5.5;	N, 10.8

The trinitrobenzene complex, prepared in methanol, crystallised in

beautiful, slender, dark blue needles, m.p. 147° (decomp.)

Analysis

	Found:	N, 14.8
$C_{24} H_{17} N_5 O_6$	requires:	N, 14.9

Preparation of 11 H-indeno[1,2-b]quinoxaline

Perkin, Roberts and Robinson, J., 1912, 101, 232.

2-Hydroxyiminoindan-1-one (Gabriel and Stelzner, Ber., 1896, 29, 2604) (0.5 g) was mixed with 40% aqueous formaldehyde solution (40 ml) to a white paste and then concentrated hydrochloric acid (ca. 40 ml) was gradually added with stirring until the solid became yellow. To complete the reaction, the solution was warmed for 10 minutes at 60° and the deep yellow indan-1,2-dione (3.7g) then collected and washed with water. It crystallised from benzene (1)/ light petroleum (1) in golden-yellow plates, m.p. 105 - 115° (lit. m.p. 95-115°).

The indenoquinoxaline separated in an almost quantitative yield when concentrated methanolic solutions of equimolecular proportions of indan-1,2-dione (4 g) and o-phenylenediamine (3 g) were mixed in the cold. It was recrystallised from methanol as colourless needles, m.p. 165-166°. Clemo and Felton (J., 1952, 1661) give m.p. 166-167°; Perkin, Roberts and Robinson give 164-165°.

Preparation of the methiodide of 11H-indeno[2,1-b]quinoxaline

A suspension of the foregoing indenoquinoxaline (1.5 g) in methyl iodide

(10 ml) was heated in a sealed Carius tube for 2.5 hours at 110-120°. After cooling, the crude orange-brown methiodide (1.7 g) was collected and thoroughly washed with hot benzene.

A suspension of the salt in cold ethanol gradually acquired a faint purple coloration; on heating all the solid dissolved giving an intensely purple-violet solution of the anhydro-base.

Preparation of 10-methylindeno[2,1-b]quinoxaline

A suspension of the methiodide (1.5 g) in chloroform (300 ml) was shaken with dilute aqueous ammonia solution. The purple-violet chloroform layer was washed with water and extracted with 10% hydrochloric acid (3 x 100 ml). The yellow, blue fluorescing, acid extracts were basified with aqueous ammonia. The precipitated dark violet solid was extracted with chloroform and the deep purple-violet layer collected, washed with water and dried over two successive portions of anhydrous sodium sulphate (3 hr.). The solution was concentrated at 60-70° under reduced pressure in an atmosphere of nitrogen. To the ice-cooled residue a little methanol was added and the dark violet solid (1.0 g), which soon separated, was collected and washed with methanol. The deep violet, almost black, irregular crystals of 10-methylindeno-[2,1-b]quinxaline gradually softened over 120° and finally melted at 128 - 130°.

The 2,4,7-trinitrofluorenone derivative was prepared by mixing a hot concentrated ethanolic solution of the pseudoaza-azulene (0.3 g in

60 ml) with a hot benzene solution of the reagent (0.4 g in 20 ml). On cooling a dark crystalline mass filled the flask. It was collected and washed with ethanol. The solid crystallised from a large volume of ethanol in very fine thread-like needles, which melted sharply at 193°.

Analysis

Found:	C, 63.9;	H, 3.2;	N, 12.5
$C_{29}H_{17}N_2O_7$ requires:	C, 63.6;	H, 3.1;	N, 12.8

Preparation of di (10-methylindeno[2,1-b] quinoxalin-11-yl)

The crude 10-methylindeno[2,1-b]-quinoxaline (0.5 g) in ethanol (200 ml) was boiled under reflux for 10 minutes. The solution was filtered hot and left standing, open, in darkness for one month (R.T.). During that period long, dark, needle-like crystals of di-(10-methylindeno[2,1-b]quinoxalin-11-yl) were gradually deposited, while the colour of the solution changed from purple-violet to blue. After one month the transformation appeared virtually complete and the solid was filtered off (0.39 g) and recrystallised from a large volume of ethanol as long needles which were dark blue by transmitted light, m.p. 324°.

Analysis

Found:	C, 83.1;	H, 5.1;	N, 11.8
$C_{32}H_{22}N_4$ requires:	C, 83.1;	H, 4.8;	N, 12.1

Molecular Weight

Found (by mass spectrometer) : 462

$C_{32}H_{22}N_4$ requires : 462.6

Preparation of 10a, 11-dihydro-10a-hydroxy-benzo[b]indeno[1,2-e]-[1,4]-thiazine hydrochloride

Indan-1,2-dione (0.80 g) was added to the colourless solution of o-aminothiophenol (0.69 g) in 2N hydrochloric acid (30 ml). On shaking, a yellow crystalline mass filled the flask and after warming at 40 - 50° for 15 minutes the solid was filtered off and washed with a little dilute hydrochloric acid. The hydrochloride (1.44 g) crystallised from acetone in thick, yellow prismatic needles, m.p. 145-146° (decomp.)

Analysis

Found: C, 61.5; H, 3.8; Cl, 12.5; N, 5.0; S, 11.4

$C_{15}H_{12}ClNOS$ requires: C, 62.2; H, 4.2; Cl, 12.3; N, 4.8; S, 11.1

Preparation of 10a, 11-dihydro-10a-hydroxy-benzo[b]indeno[1,2-e]-[1,4]-thiazine.

(a) A solution of indan-1,2-dione (0.40 g) and o-aminothiophenol (0.35 g) in ethanol (30 ml) was boiled under reflux for 15 minutes in the presence of a small quantity of piperidine acetate. On cooling the solution deposited a colourless crystalline solid (0.34 g) which was recrystallised from ethanol as colourless prismatic needles.

The crystals acquired a slight pink coloration on warming and became distinctly reddish near their melting point which depended upon the rate of heating. When the temperature was raised slowly the pseudo-base melted at 211 - 212° (with decomposition to a red oil).

Analysis

Found: C, 71.4; H, 4.45; N, 5.3; S, 12.5

$C_{15}H_{11}NOS$ requires: C, 71.1; H, 4.4; N, 5.5; S, 12.7

(b) The hydrochloride was shaken with dilute aqueous ammonia and the resulting cream coloured solid filtered off and washed with water and ethanol. It crystallised from ethanol in colourless needles, m.p. 210 - 212° (with decomposition to a red oil), which did not depress the m.p. of the pseudo-base obtained as in (a).

Analysis

Found: C, 70.9; H, 4.4; N, 5.4; S, 12.4

$C_{15}H_{11}NOS$ requires: C, 71.1; H, 4.4; N, 5.5; S, 12.7

Preparation of benzo[b]indeno[1,2-e]-[1,4]- thiazine and di (benzo[b]-indeno[1,2-e]-[1,4]-thiazin-11-yl).

(All distillations were carried out under nitrogen)

I. Benzo[b]indeno[1,2-e]-[1,4]-thiazine.

(a) A suspension of the foregoing hydrochloride (1,12 g) in approximately 0.2N hydrochloric acid (60 ml) was boiled for 3 minutes. The solution at first became faintly pink and then pale yellow and the

particles of the yellow solid gradually darkened and aggregated into clumps. When boiling was stopped the suspension was immediately cooled in ice-water and the crude reddish-brown solid collected and washed with dilute sodium carbonate solution and water. The dried material (0.88 g) was dissolved in benzene, and after filtering off a little dark residue, chromatographed on an alumina column (30 x 3 cm). A brown, strongly adsorbed, impurity was retained at the top of the column. Development with benzene (5)/light petroleum (2) gave three coloured zones:

(i) very intense red
(ii) diffuse violet
(iii) very faint red

Elution with the same solvent first yielded a deep red eluate of benzo[b]indeno[1,2-e]-[1,4]-thiazine (fraction 1) and then a more dilute violet eluate of di(benzo[b]indeno[1,2-e]-[1,4]-thiazin-11-yl) (fraction 2). Continued elution with benzene gave a large volume of a very dilute pink solution of the third basic compound "C" (Reaction Scheme I) (fraction 3).

Fraction 1.

The deep red eluate was concentrated to a small volume, and after addition of a little methanol, the cooled solution deposited a reddish-black crystalline solid which was collected and washed with methanol. The benzoindenothiazine (90 mg) was recrystallised from ethanol as reddish-black prismatic needles which were dark red by transmitted light, m.p. 169.5° - 170°.

Analysis

Found:	C, 76.3;	H, 3.9;	N, 6.2;	S, 13.4
$C_{15}H_9NS$ requires:	C, 76.55;	H, 3.9;	N, 5.95;	S, 13.6

Fraction 2.

Evaporation of the violet eluate yielded a violet-black solid (18 mg). It was recrystallised from benzene (4)/chloroform (1) as violet-black prisms which did not melt up to 350°; on admixture with the di(benzo[b]indeno[1,2-e]-[1,4]- thiazin-11-yl) obtained as in II below, the resulting material still did not melt up to 350°.

Fraction 3.

Concentration of the pink solution gave a minute quantity of dark red solid, which did not possess a definite m.p. but decomposed over the range 255-265°.

I. Benzo[b]indeno[1,2-e]-[1,4]-thiazine.

(b) The pseudo-base (0.20 g) was heated at ca. 210° for 1-2 minutes. The dark red residue was extracted with benzene (1)/light petroleum (1) and filtered through an alumina column. A brown, strongly adsorbed impurity was retained at the top of the column and development with the same solvent gave a single deeply coloured zone. After addition of methanol the concentrated deep red eluate deposited reddish-black crystals (40 mg). The compound crystallised from ethanol as reddish-black needles, m.p. 169.5 - 170°, which did not depress the m.p. of benzo [b]indeno-[1,2-e]-[1,4]-thiazine obtained as in (a).

II. Di(benzo[b]indeno[1,2-e]-[1,4]-thiazin-11-yl).

A suspension of the hydrochloride (0.54 g) in 2N hydrochloric acid (25 ml) was boiled for 5 minutes and then kept at 80-90° for ca. 30 minutes. The solution became greenish and the solid gradually darkened and eventually amost black particles settled at the bottom. They were then collected and washed successively with dilute hydrochloric acid (until the washings were colourless), dilute ammonia and water.

The crude dried material (0.41 g) was dissolved in benzene (4)/chloroform (1) and chromatographed on a column as described in I(a). Three deeply coloured fractions were again obtained, but this time fraction 2 (violet eluate) represented the main product.

Fraction 1.

Evaporation of the red eluate yielded a reddish-black solid (8 mg). It crystallised from ethanol as prismatic needles which were dark red by transmitted light, m.p. 169° - 170°, not depressed on admixture with the benzoindenothiazine obtained as in I(a).

Fraction 2.

The concentrated violet eluates deposited violet-black solid which was collected and washed with benzene. Di(benzo[b]indeno[1,2-e]-[1,4]-thiazin-11-yl) (85 mg) crystallised from benzene (4)/chloroform (1) in violet-black prisms which did not melt up to 350°.

Analysis

Found: C, 76.8; H, 3.4; N, 6.0; S, 13.6

$C_{30} H_{16} N_2 S_2$ requires: C, 76.9; H, 3.4; N, 6.0; S, 13.7

Molecular Weight

Found (by mass spectrometer) : 468

$C_{30} H_{16} N_2 S_2$ requires: 468.6

Fraction 3.

Removal of solvent gave a very small quantity of dark red solid (Compound "C"); Reaction Scheme I) which crystallised from benzene in red plates. It did not show a definite melting point but decomposed over the range 260 - 269°.

Analysis

Found: Cl, 18.1

Monochloro derivative of benzo[b]indeno[1,2-e]-[1,4]-thiazine ($C_{15} H_8 Cl NS$) requires: Cl, 13.2

Dichloro derivative ($C_{15} H_7 Cl_2 NS$) requires: Cl, 23.3.

Preparation of ethyl γ-phenyl-α-acetylacetoacetate.

Viscontini and Merckling, Helv. Chim. Acta, 1952, 35, 2280.

Magnesium turnings (27 g, 1.1 m.) and ethanol (150 ml) were allowed to react at R.T. with exclusion of moisture. The reaction

was started by addition of carbon tetrachloride (5 ml) and when it became vigorous, dry ether (1 l.) was added gradually. When after ca. 3 hours the reaction ceased, ethyl acetoacetate (130 g, 1 m.) diluted with ether (200 ml) was introduced slowly with ice cooling and stirring. With the reaction vessel immersed in ice-salt mixture and vigorous stirring, phenylacetyl chloride (155 g, 1m.) dissolved in ether (200 ml) was added to the solution of the magnesium complex. A white precipitate appeared; the solution was stirred for a further one hour at R.T. and was then left standing overnight. After addition of ice and acidification (dilute H Cl), the precipitate dissolved and an ether layer separated. The latter was collected, washed with water and dried over anhydrous sodium sulphate. Removal of solvent gave ethyl γ-phenyl-α-acetylacetoacetate (220 g; 89%), as a pale yellow, viscous oil which was sufficiently pure for the following reaction (preparation of the β-ketoester). A sample was distilled, b.p. 155-156°/0.4 mm.

Preparation of ethyl (or methyl) γ-phenyl-acetoacetate

(a) cf. Viscontini and Adank, Helv. Chim. Acta, 1952, 35, 1342.

5% Ethanolic ammonia (270 ml) was slowly added to ethyl γ-phenyl-α-acetylacetoacetate (50 g) at 0°. When the addition was complete, a little water (3 ml) was introduced and the solution left standing overnight. Ice and dilute sulphuric acid were added to the concentrated solution and the yellow oil extracted with ether. The extract was washed

with sodium carbonate solution and water and dried over anhydrous sodium sulphate. Removal of solvent gave a viscous oil which on distillation gave two main fractions. The first fraction, boiling range 60 - 70°/0.5 mm was discarded; the second fraction, b.p. 110-112°/0.7 mm, consisted of pure ethyl γ-phenylacetoacetate (21 g; 51%). Sonn and Litten (Ber., 1933, 66B, 1512) give b.p. 153-155°/9 mm.

The ester was characterised as its copper salt, prepared by shaking an ethereal solution of the ester with an aqueous solution of copper acetate. The salt crystallised from benzene in blue crystals, m.p. 177-178° (lit. m.p. 176 - 178°), the semicarbazone crystallised from ether in colourless needles, m.p. 114-116° (lit. m.p. 114-116°).

(b) Hunsdiecker, Ber., 1942, 75, 454.

Ethyl γ-phenyl-α-acetylacetoacetate (124 g) was gradually introduced to a methanolic solution of sodium methoxide (prepared by addition of sodium (12.5 g) to dry methanol (350 ml)). After standing overnight at room temperature the solution was poured into dilute hydrochloric acid (1.5 l.) and extracted with ether. The extract was washed with sodium carbonate solution and water and dried over anhydrous sodium sulphate. Removal of solvent yielded a viscous yellow oil which was separated by distillation into two fractions. The first fraction, boiling range 65 - 78°/0.3 mm, was discarded.

Methyl γ-phenylacetoacetate (68 g; 71%), b.p. 99 - 100°/0.3 mm, was obtained as a colourless oil (fraction 2).

Preparation of methyl γ-phenyl-α-phenacylacetoacetate

cf. Weidlich and Daniels, Ber., 1939, 72B, 1590.

To a suspension of finely divided sodium (7.8 g) in dry ether (400 ml), a solution of methyl γ-phenylacetoacetate (65 g) in dry ether (100 ml) was added gradually with stirring. The mixture was boiled under reflux for 6 hours when a large white mass of the sodium compound separated. Phenacyl bromide (67.5 g) was added to the cold solution and the boiling under reflux continued for 4 hours. After acidication with dilute hydrochloric acid, the ether layer was separated, washed with sodium carbonate and water and dried over anhydrous sodium sulphate. Removal of solvent gave methyl γ-phenyl-α-phenacylacetoacetate (96 g, 91%) as a viscous orange oil. The ester was used for the preparation of 2,3-diphenylcyclopent-2-enone without purification.

Preparation of 2,3-diphenylcyclopent-2-en-one

cf. Winternitz, Mousseron, and Rouzier, Bull Soc. chim. France, 1953, 196.

A 5% solution of sodium hydroxide (1 l.) was heated on the water-bath in a stream of nitrogen and when its temperature reached

95°, a solution of methyl γ-phenyl-α-phenacylacetoacetate (55 g) in ethanol (150 ml) was added dropwise with stirring, the temperature being maintained at 95°. When the addition of ester was complete, the mixture was heated for 30 minutes on a boiling water-bath and then boiled for a further 5 minutes. The orange oil was extracted with chloroform and the extract washed with water and dried over anhydrous sodium sulphate. Removal of solvent gave a dark viscous residue which was distilled in vacuo. The diphenylcyclopentenone was obtained as a pale yellow oil, b.p. 162 - 164/0.5 mm, which solidified on mixing with ether; yield of the solid, 28.5 g. (69%). It crystallised from methanol as colourless prisms, m.p. 95-96°. Borsche and Klein (Ber., 1939, 72B, 2082) describe the ketone as crystallising from methanol in yellowish leaflets, m.p. 95°. The 2,4-dinitrophenylhydrazone crystallised from acetic acid as dark red prisms, m.p. 226° (lit. m.p. 226°).

Preparation of 2,3-diphenylcyclopenta[b]quinoline-9-carboxylic acid.

cf. Los and Stafford, J., 1959, 1680.

Solutions of isatin (3.2 g) in 30% potassium hydroxide solution (20 ml) and 2,3-diphenylcyclopent-2-enone (5.0 g) in ethanol (40 ml) were mixed and heated under reflux for 8 hours. The solution was poured into water (200 ml) and addition of 50% acetic acid precipitated a yellow solid which was collected and washed with water (500 ml) and

ethanol (100 ml). The 2,3-diphenylcyclopenta-[b]quinoline-9-carboxylic acid (6.2 g) was sufficiently pure for most purposes but crystallised from a large volume of benzene as pale yellow needles, m.p. 324°.

Analysis.

	Found:	C, 82.2;	H, 4.9;	N, 4.1
$C_{25}H_{17}NO_2$	requires:	C, 82.6;	H, 4.7;	N, 3.9

Methylation of 2,3-diphenylcyclopenta[b]-quinoline-9-carboxylic acid

The acid (4.0 g) in absolute methanol (140 ml) and concentrated sulphuric acid (15 ml) was boiled under reflux for 2 days. The solution was then poured into an excess of 10% sodium carbonate solution and extracted with chloroform. The blue-fluorescent extract was washed with water and dried over anhydrous sodium sulphate. Removal of solvent gave the pale yellow, crystalline ester (3.2 g; 80%). It was recrystallised from methyl acetate as long, slender, pale yellow needles, m.p. 207.5 - 208°.

Analysis.

	Found:	C, 82.9;	H, 5.4;	N, 3.9
$C_{26}H_{19}NO_2$	requires:	C, 82.7;	H, 5.1;	N, 3.7

Preparation of 2,3-diphenyl-4-methyl-9-carbomethoxycyclopenta[b]quinoline.

2,3-Diphenyl-9-carbomethoxycyclopenta[b]quinoline (methyl 2,3-diphenylcyclopenta[b]quinoline-9-carboxylate) (1.2 g) in benzene

(35 ml) and dimethyl sulphate (15 ml) was boiled under reflux for 4 hours. The orange solution was diluted with more benzene (200 ml) and the methosulphate extracted with 10% acetic acid (shaking with water causes partial conversion to the anhydro-base). The extract was basified with sodium carbonate solution and the precipitated dark blue solid extracted with chloroform. The chloroform layer was separated, dried over anhydrous sodium sulphate, and evaporated (under nitrogen) to a small volume. After addition of a little methanol, the cooled solution deposited 2,3-diphenyl-4-methyl-9-carbomethoxycyclopenta[b]quinoline (0.45 g) as blue-black crystals. It was recrystallised from a large volume of methanol as blue-black prismatic needles, which were dark blue by transmitted light, m.p. 178.5 - 179°.

Analysis

Found: C, 83.1; 5.7; N, 3.3

$C_{27}H_{21}NO_2$ requires: C, 82.8; 5.4; N, 3.6

The trinitrobenzene complex crystallised from ethanol saturated with trinitrobenzene in blue-black prisms, m.p. 130 - 131°.

Found: N, 8.9. $C_{33}H_{24}N_4O_8$

requires: N, 9.3.

Decarboxylation of 2,3-diphenylcyclopenta-[b]quinoline-9-carboxylic acid: Preparation of 2,3-diphenyl-4-methylcyclopenta[b]quinoline.

A mixture of soda-lime (4 g) and 2,3-diphenylcyclopenta[b]-quinoline-9-carboxylic acid (1 g) was covered with soda-lime (2 g) in a hard-glass tube attached to a U-tube immersed in ice-water and evacuated (water-pump). The tube was heated, gently at first, then strongly. No product collected in the U-tube but a brown crust gradually formed on the upper part of the reaction vessel. The solid was extracted with ether and the extract washed with sodium carbonate solution and water and dried over anhydrous sodium sulphate. Removal of solvent yielded a very dark solid which was dissolved in benzene and chromatographed on alumina, using benzene (1)/light petroleum (1) as developer. A brown strongly adsorbed band was retained at the top of the column. Continued development gave two strongly fluorescing zones, which were eluted with the same solvent.

(I) Concentration of the first, pale blue-fluorescing eluate yielded 2,3-diphenylcyclopenta[b]quinoline as a buff solid which soon darkened and could not be purified. It was, therefore, directly converted to the methosulphate by boiling under reflux for 3 hours in benzene with a large excess of dimethyl sulphate. The pale orange, strongly fluorescing solution was extracted with very dilute hydrochloric acid and the pale yellow extract basified with sodium carbonate solution and shaken with chloroform. The chloroform layer was separated, dried

($Na_2 SO_4$), and evaporated to give a reddish-purple residue, which formed a trinitrobenzene complex in ethanol. The complex was recrystallised from ethanol, saturated with trinitrobenzene, as purple-black prisms, m.p. 135 - 136°.

Analysis

Found:	C, 68.5;	H, 3.9;	N, 10.0
$C_{31} H_{22} N_4 O_6$ requires:	C, 68.1;	H, 4.0;	N, 10.3

(II) Elution of the second fluorescing zone gave a pale yellow solution. Removal of solvent yielded a golden-yellow solid which crystallised from ethanol in yellow needles, m.p. 228 - 229° (with sublimation and decomposition to a red oil).

Analysis

Found:	C, 87.3;	H, 4.8;	N, 3.9.

The solid was boiled under reflux in benzene in the presence of a large excess of dimethyl sulphate, but the resulting pale orange solution gave no purple or blue colour on treatment with basic reagents. Ethanolic and benzene solutions of the yellow solid exhibited a striking blue-violet fluorescence; on addition of hydrochloric acid to the ethanolic solution the fluorescence changed to yellowish-blue.

Attempted decarboxylation of 2,3-diphenylcyclopenta[b]quinoline-9-carboxylic acid in quinoline in the presence of copper bronze.

A solution of the acid (0.50 g) in quinoline was heated for 2

hours at ca. 240° in the presence of copper bronze. The deep red solution was steam-distilled and the residue extracted with ether. The ether layer was washed with water, dried and evaporated to give a dark red gummy solid which was chromatographed on alumina using benzene as solvent. Development with benzene (1)/light petroleum (1) gave two coloured zones, the upper orange (showing yellow fluorescence) and the lower red (non-fluorescing).

(I) Concentration of the deep red eluates gave a reddish-black solid (0.12 g) which was collected and recrystallised from ethanol as reddish-black prisms, m.p. 291-292°.

Analysis

Found: C, 88.1; H, 5.1; N, 4.9.

Absorption Spectrum (in ethanol)

λ max. : 500, 315, 243 mμ

λ min. : 418, 286, 226 mμ

The red solid was only sparingly soluble in ethanol and was very soluble in benzene and acetic acid.

(II) The yellow eluates were evaporated to a small volume and addition of light petroleum precipitated a golden-yellow solid (0.16 g) which crystallised from ethanol in long, slender needles, m.p. 241°.

Analysis

Found: C, 86.1; H, 4.7; N, 4.3

2,3-Diphenyl-9-hydroxycyclopenta[b]quinoline ($C_{24}H_{17}NO$) requires:

C, 86.0; H, 5.1; N, 4.2.

Preparation of 2,3-diphenyl-5-salicylidenecyclopent-2-enone

cf. Borsche and Menz, Ber., 1908, 41, 202.

A solution of 2,3-diphenylcyclopent-2-enone (2.4 g) and salicyclaldehyde (1.2 ml) in ethanol (25 ml) was mixed with 10% sodium hydroxide solution (25 ml). After standing overnight the orange-red solution deposited the sodium salt of 2,3-diphenyl-5-salicylidenecyclopent-2-enone. The suspension was poured into water (200 ml) and acidified with dilute hydrochloric acid. The yellow salicylidene derivative (2.7 g) was collected and washed with water and methanol. It crystallised from methanol as pale yellow thread-like needles, m.p. 208.5 - 209°.

Analysis

Found:	C, 85.1;	H, 5.4
$C_{24}H_{18}O_2$ requires:	C, 85.2;	H, 5.35

Preparation of 2,3-diphenylbenzo[b]cyclopenta[e]pyran

A suspension of 2,3-diphenyl-5-salicylidenecyclopent-2-enone (1.5 g) in acetic acid (20 ml) and concentrated hydrochloric acid (8 ml) was boiled for one hour. The colour gradually changed from reddish-orange to reddish-brown. The cold, green-fluorescing solution was poured into water (150 ml) and the precipitated reddish-brown solid collected and washed with water. The dried material was dissolved in benzene and chromatographed on an alumina column. Development with benzene (1)/light petroleum (2) gave a number of coloured bands and the required reddish-purple zone could not be cleanly separated. The

concentrated reddish eluates were re-chromatographed using the same mixture of solvents as developer. Evaporation of the red eluate gave the pyran as a reddish-black solid (0.24 g). It crystallised from ethanol as reddish-black prisms which were dark red by transmitted light, m.p. 249 - 250°.

Analysis

Found:	C, 89.3;	H, 5.0
$C_{24}H_{16}O$ requires	C, 90.0;	H, 5.0

Determination of the "basicities" of pseudoazulenes

cf. Plattner, Heilbronner and Weber, Helv. Chim. Acta, 1949, 32, 574.

Standard aqueous solutions of sulphuric acid were prepared by weighing portions of "Anala R" acid and titrating the appropriately diluted solutions with standard borax solution using methyl red as indicator. The Hammett functions of most of the acids were obtained by interpolation from the graphs constructed from data supplied by Paul and Long (Chem. Rev., 1957, 57, 11). The Ho values given by these authors differ from those of previous tabulations (Hammett and Deyrup, J.A.C.S., 1932, 54, 2721, 4239; Hammett, "Physical Organic Chemistry", Chap. IX, New York, 1940) by small but varying amounts and for the aqueous solutions of sulphuric acid they are generally more negative by 0.10 - 0.20 unit. The Hammett functions of the very dilute acids (required for determinations of the Ho (K' = 1)

constants of compounds XLIV and LXI) could not be obtained by interpolation and were assumed to coincide with the pH values.

Partition Experiments.

The solvent system used was aqueous sulphuric acid-benzene. The optical density (D) of the unextracted benzene solution of pseudoazulene was first determined at a chosen wavelength in the visible region. The distribution of pseudoazulene between benzene and sulphuric acids of different strengths was studied by shaking 5 ml aliquots of this solution with 5 ml portions of the acids for 5 minutes and then allowing the layers to settle for a further 20 minutes (in darkness). The benzene layers were then pipetted out and their optical densities redetermined at the previously chosen wavelength.

The optical density (D') of the acid extracted solution is proportional to the concentration of pseudoazulene in the organic phase, and (D-D') is therefore proportional to the concentration of pseudoazulene in the aqueous phase. The apparent distribution coefficient K' of pseudoazulene between benzene and sulphuric acid is then given by

$$K' = \frac{D'}{D-D'}$$

The plots of $\log_{10} K'$ against Ho were linear and are given in Figs. 1-4.

Contents of the Experimental Section